Thermal Analysis
measurements

R W McCallum

Ames Laboratory

And

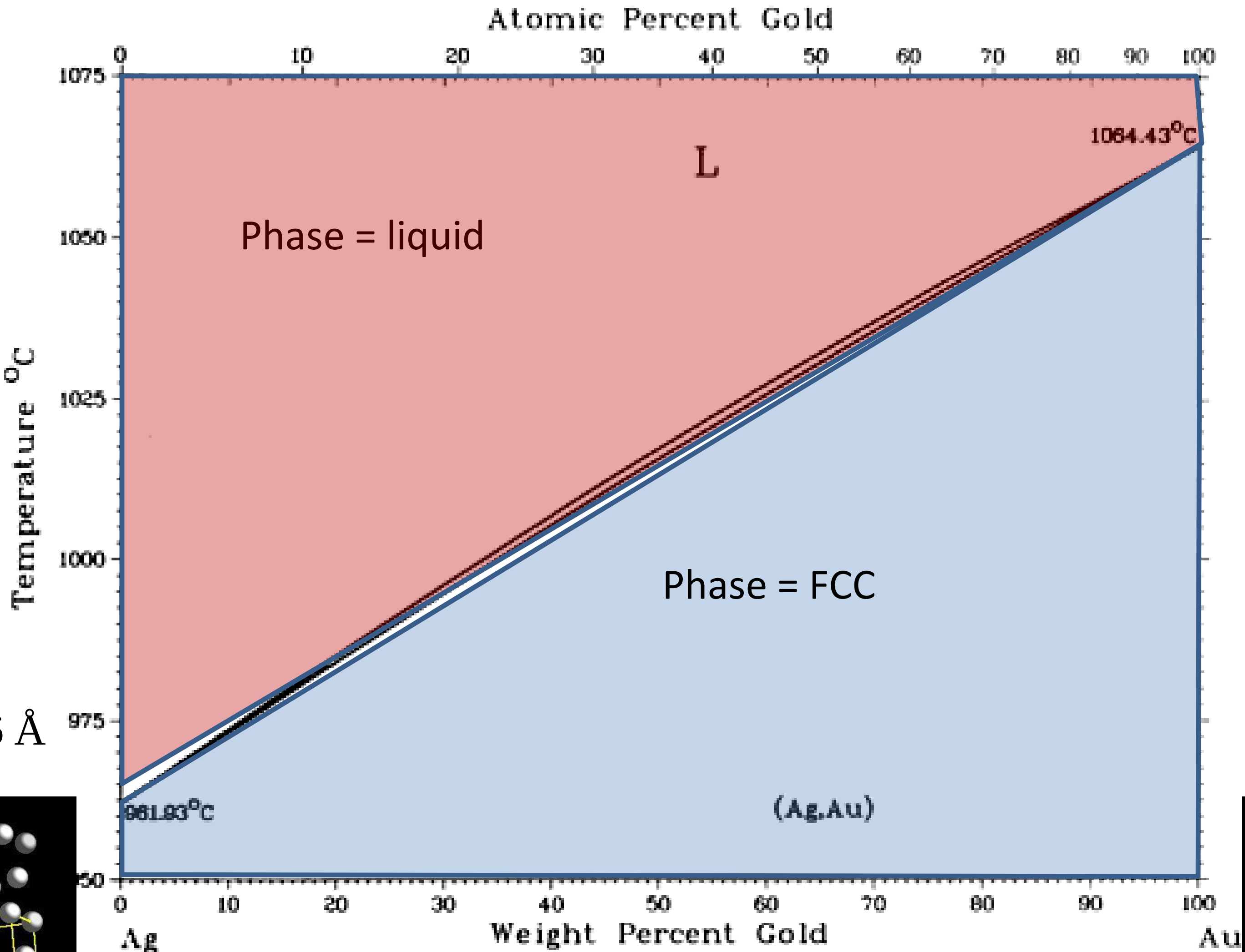
Materials Science and Engineering

Phase vs Phase Field

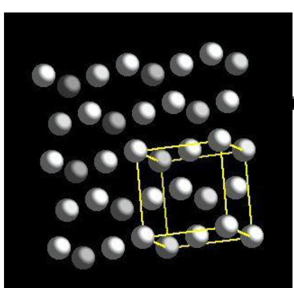
- **phase**
  - set of states of a macroscopic physical system that have relatively uniform chemical composition and physical properties (i.e. density, crystal structure, index of refraction, and so forth).
- **phase field**
  - range of temperatures and compositions over which a phase exists.

From Wikipedia,

Solid Solutions



Ag^{+1} 1.26 Å



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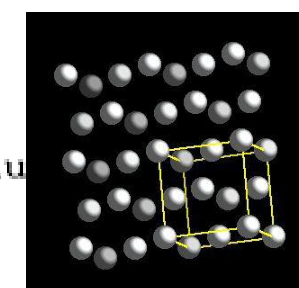
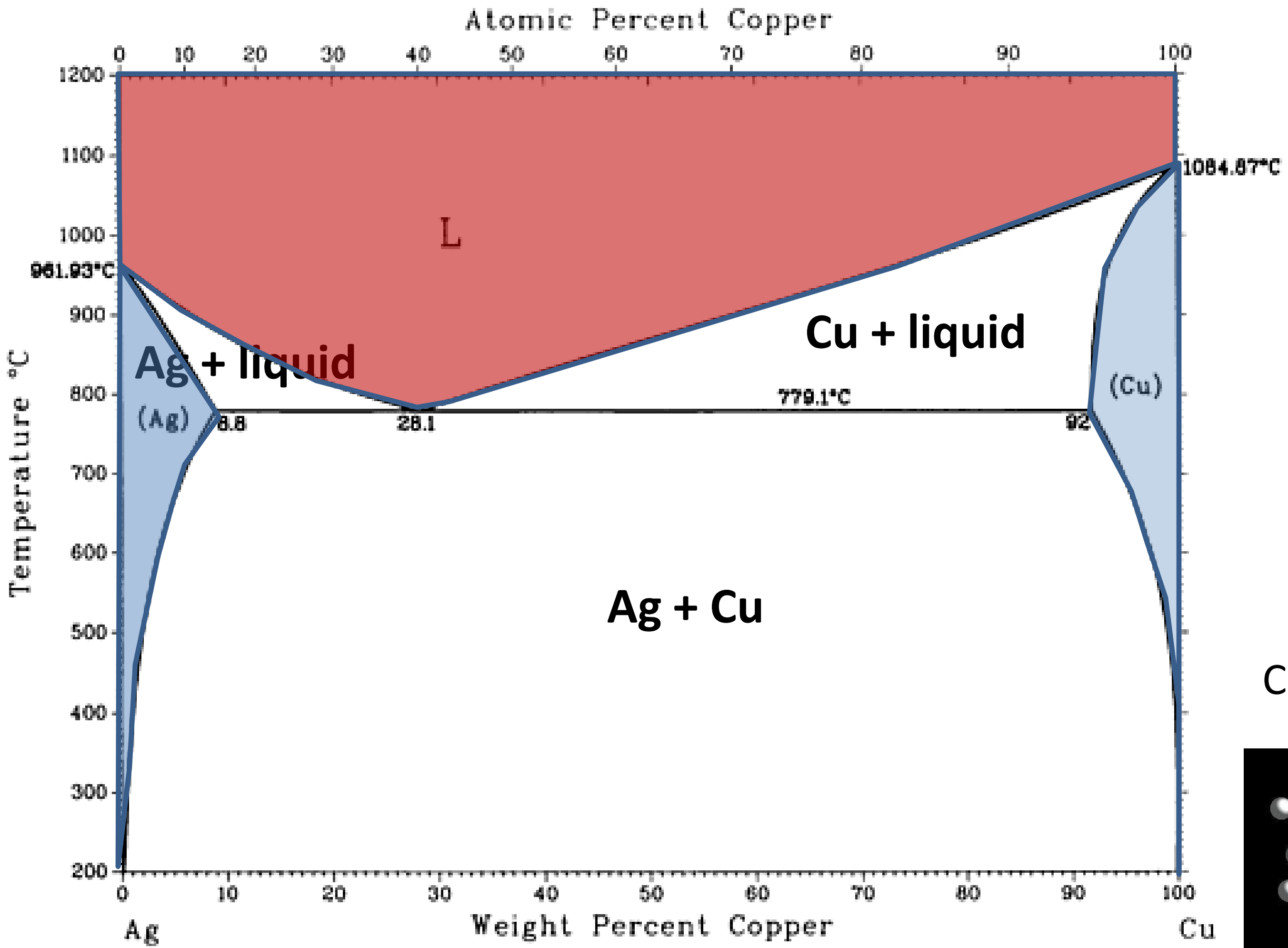
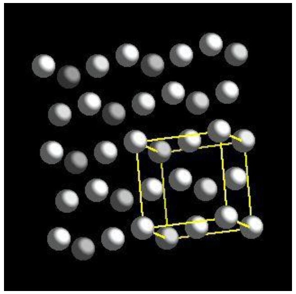


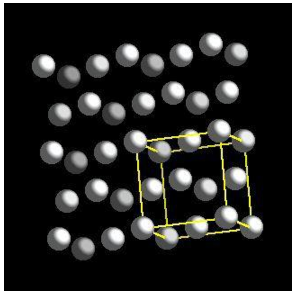
Eutectic Phase Fields



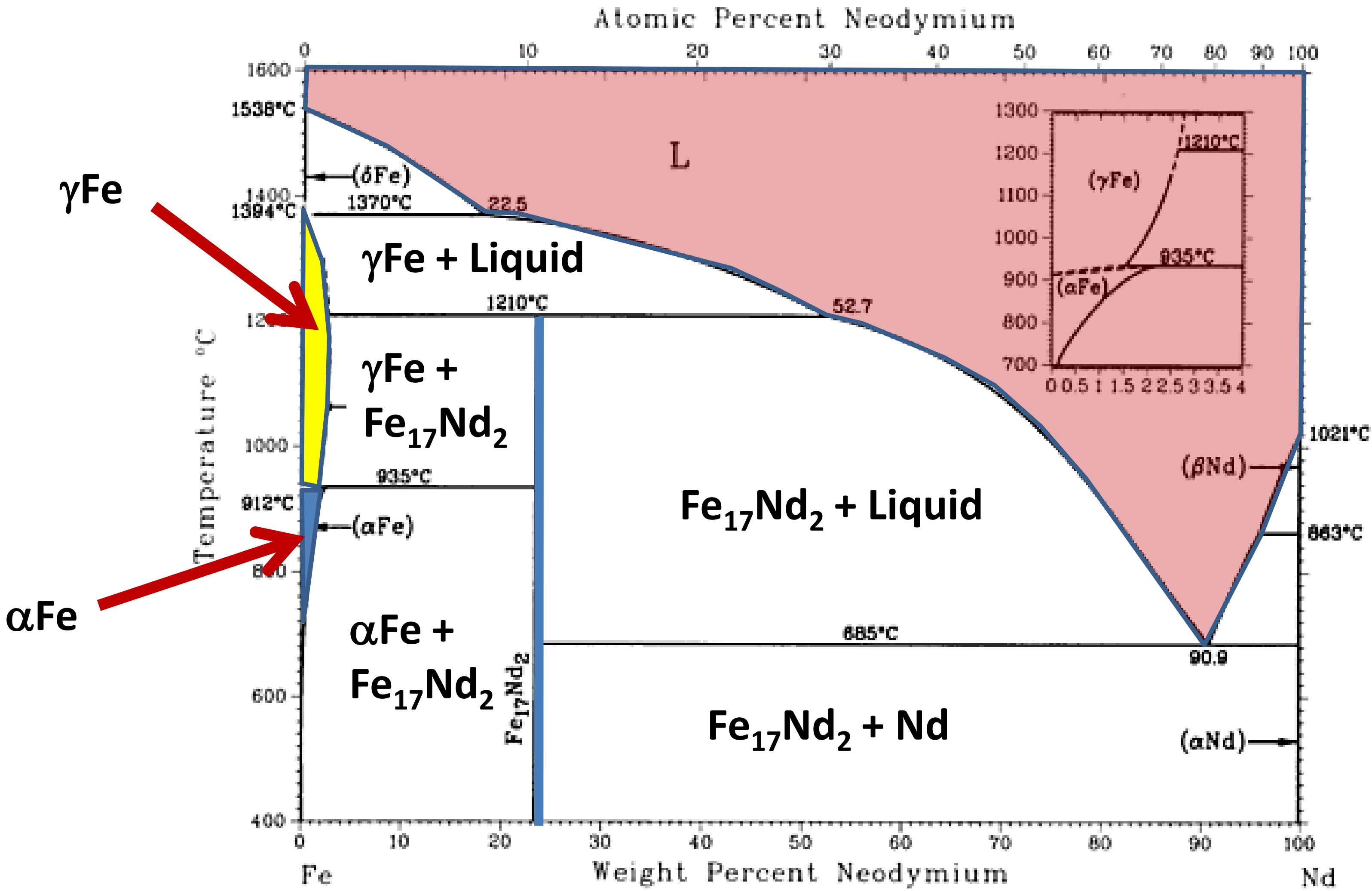
Ag^{+1} 1.26 Å



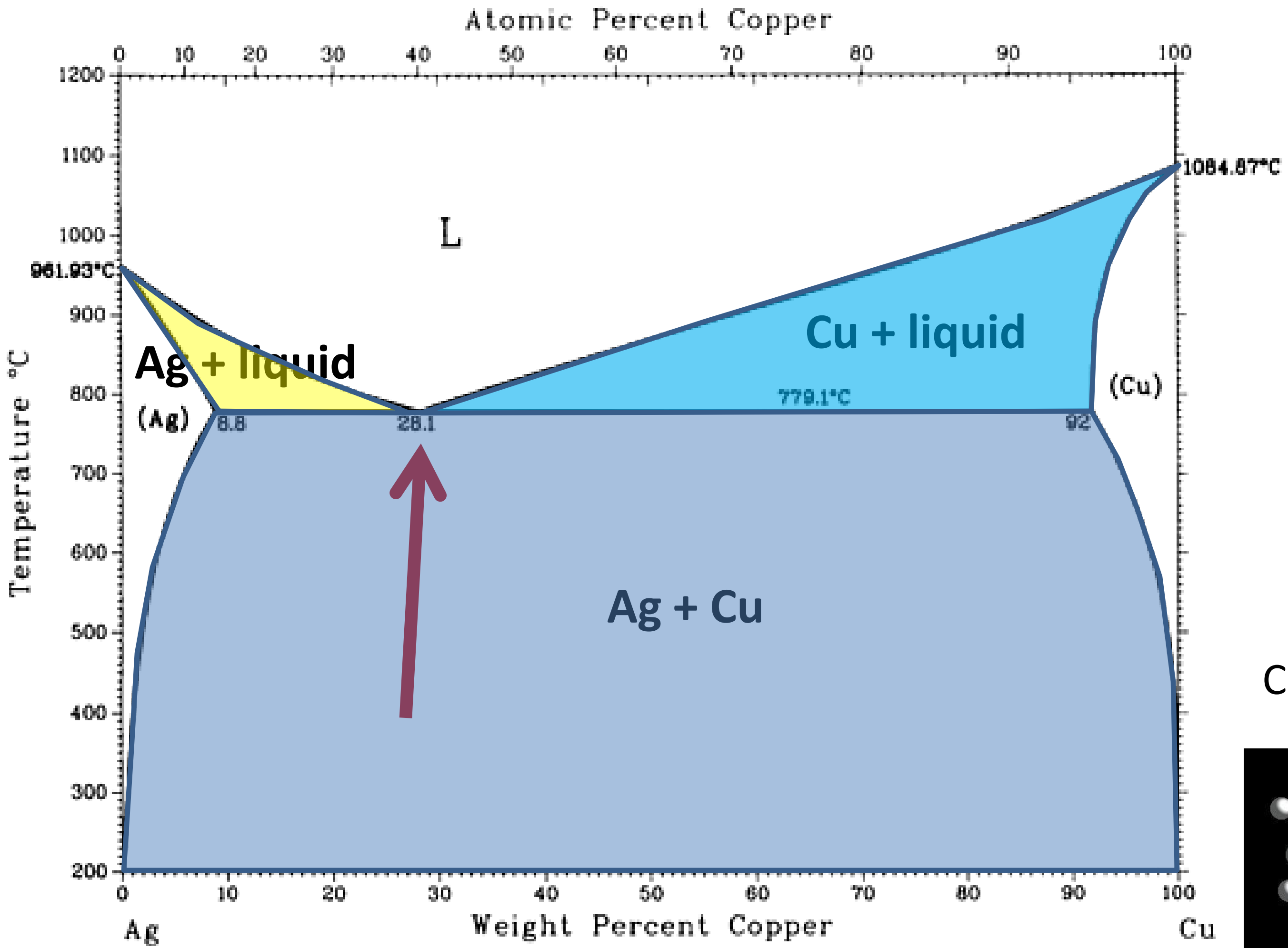
Cu^{+1} 0.96 Å



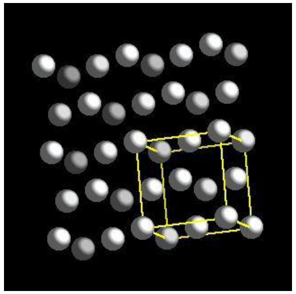
Nd – Fe Phase Fields



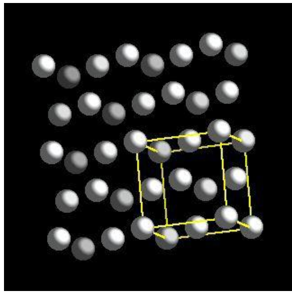
Eutectic 2 phase regions



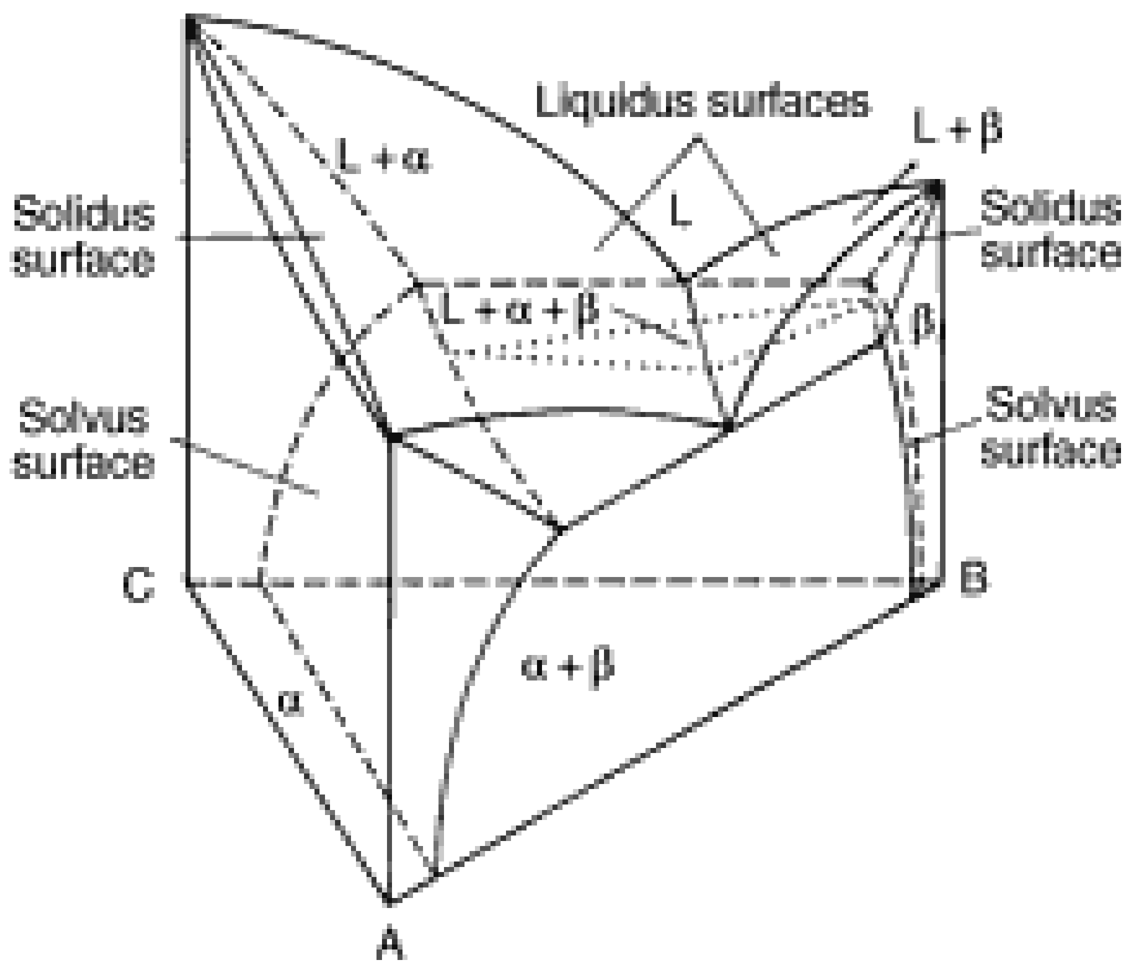
Ag^{+1} 1.26 Å



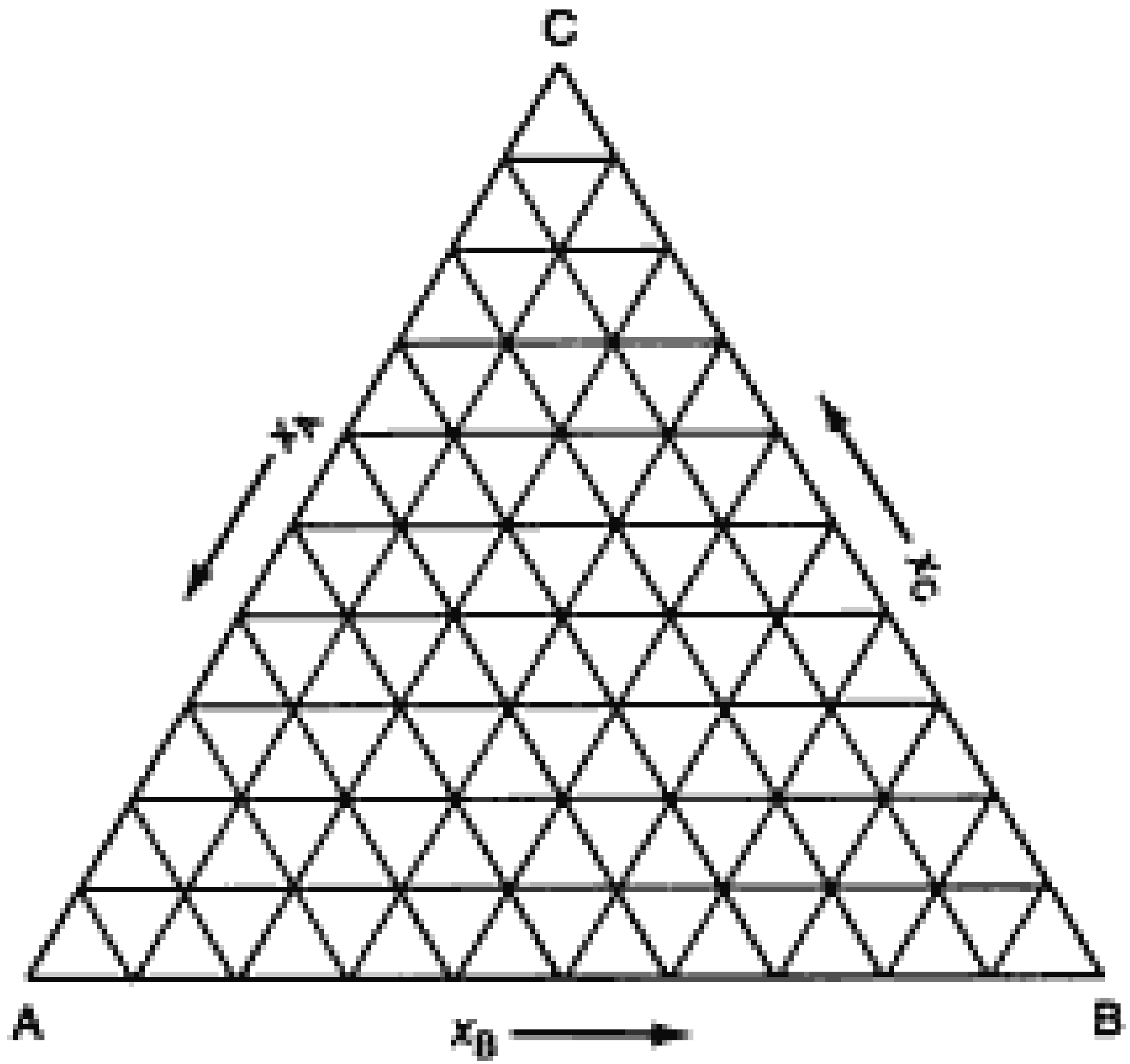
Cu^{+1} 0.96 Å



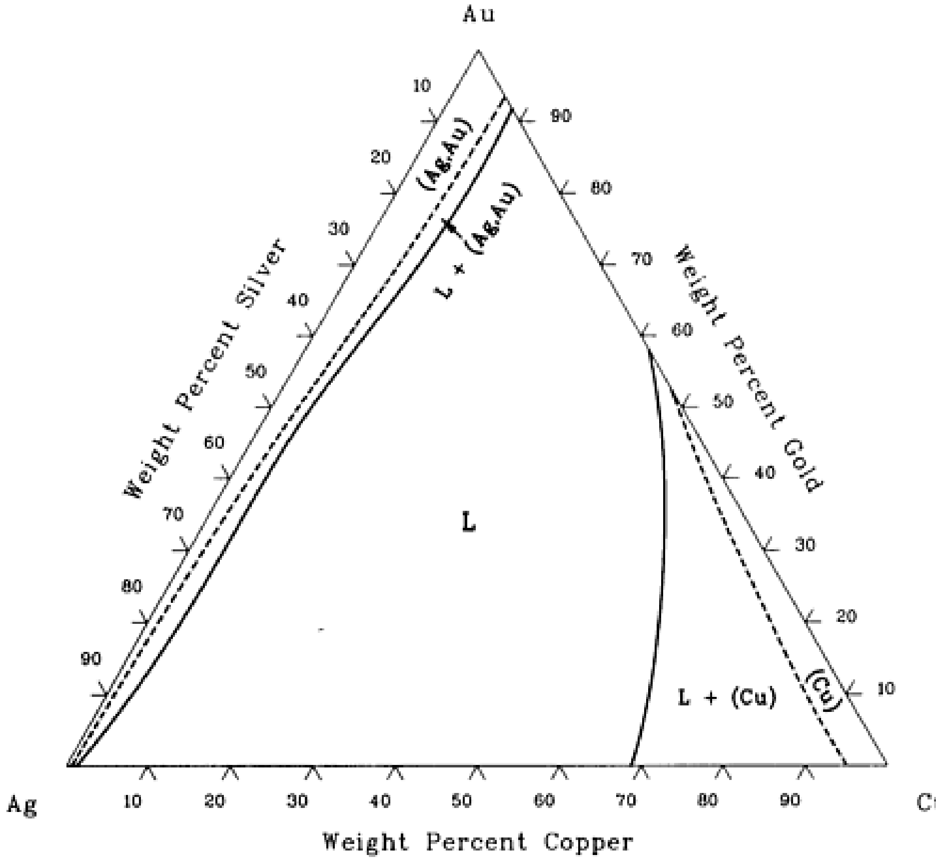
Ternary Phase Diagram



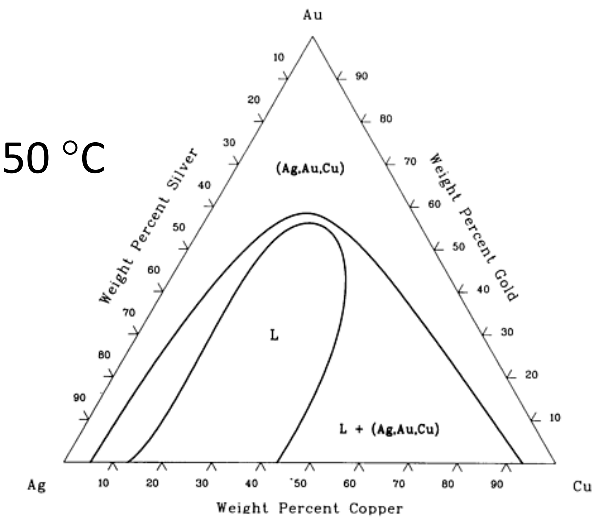
Ternary Isothermal Cut



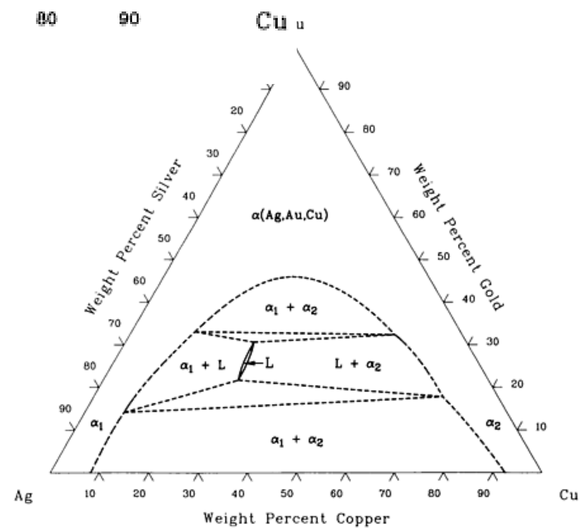
Ag-Au-Cu



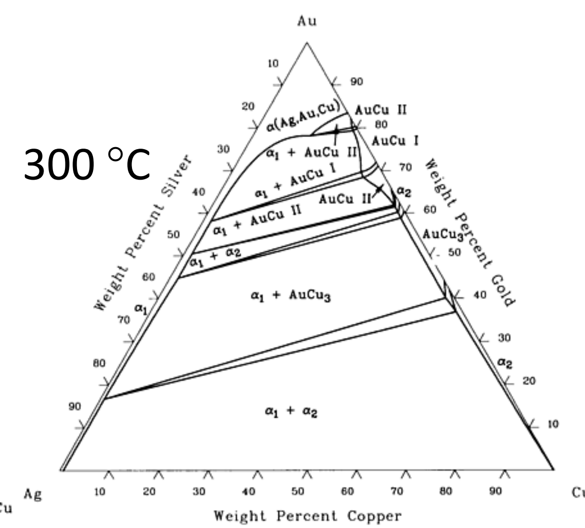
850 °C



775 °C

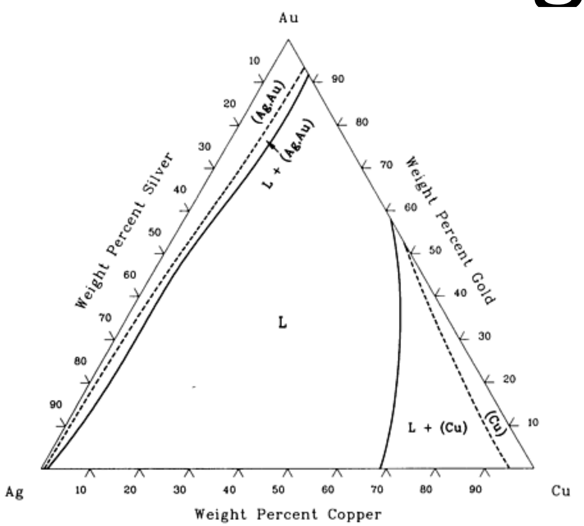


300 °C

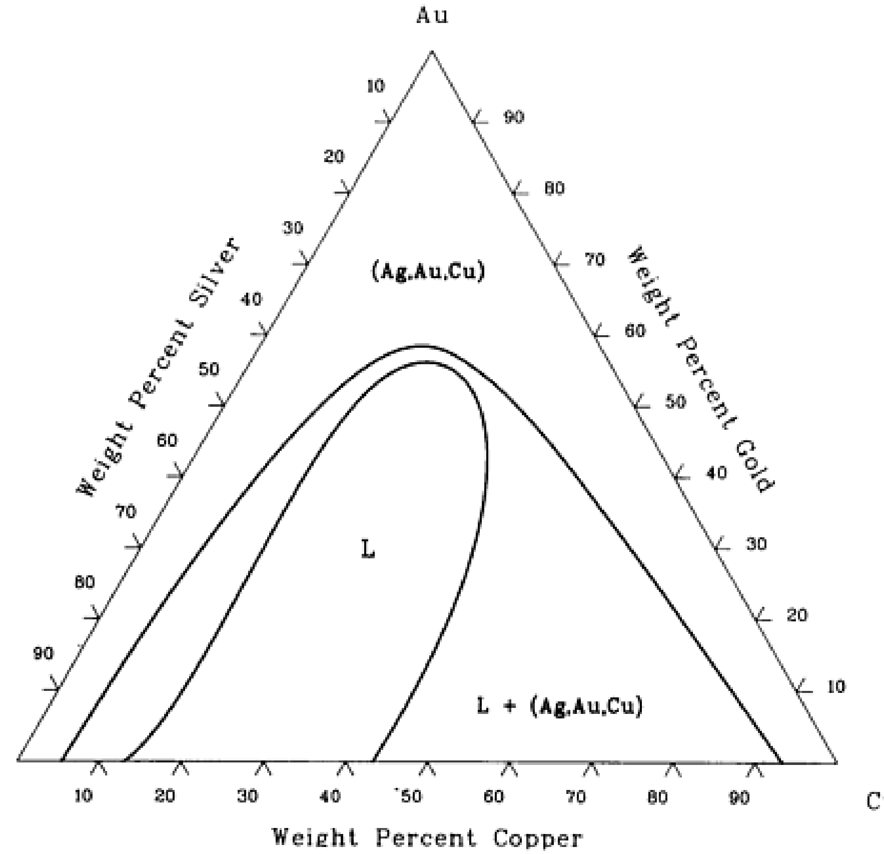


Ag-Au-Cu

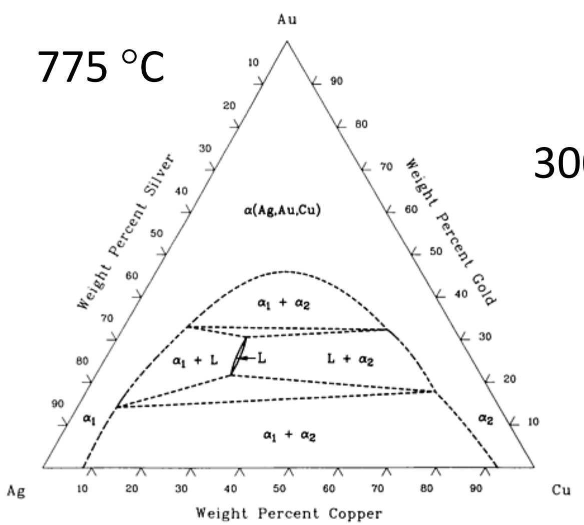
950 °C



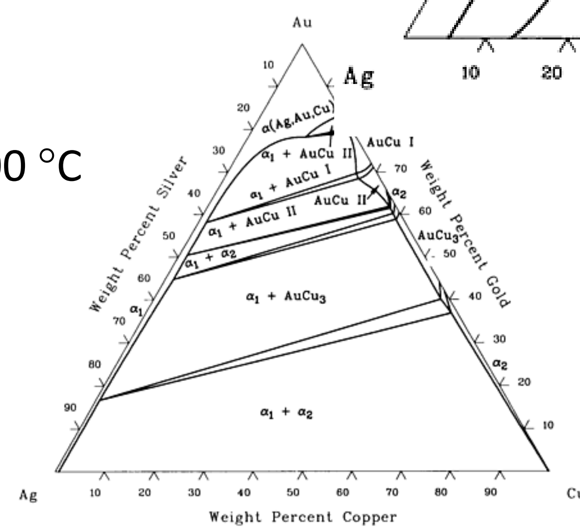
850 °C



775 °C

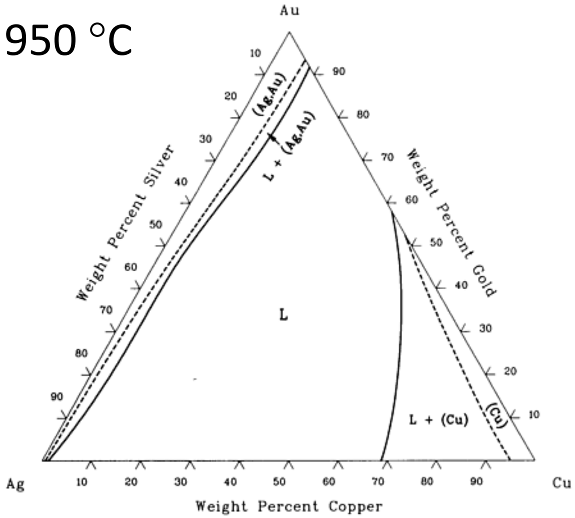


300 °C

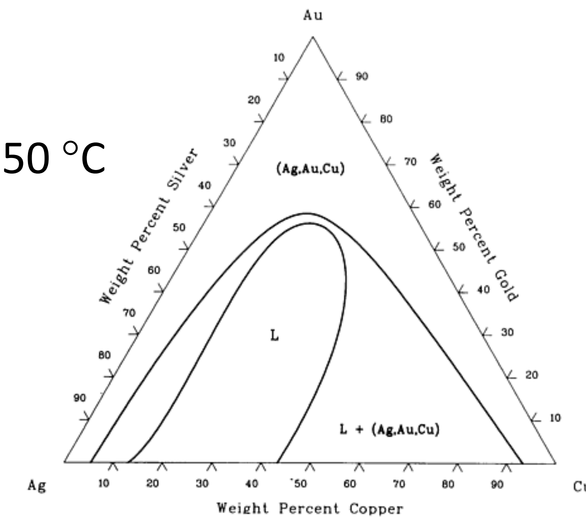


Ag-Au-Cu

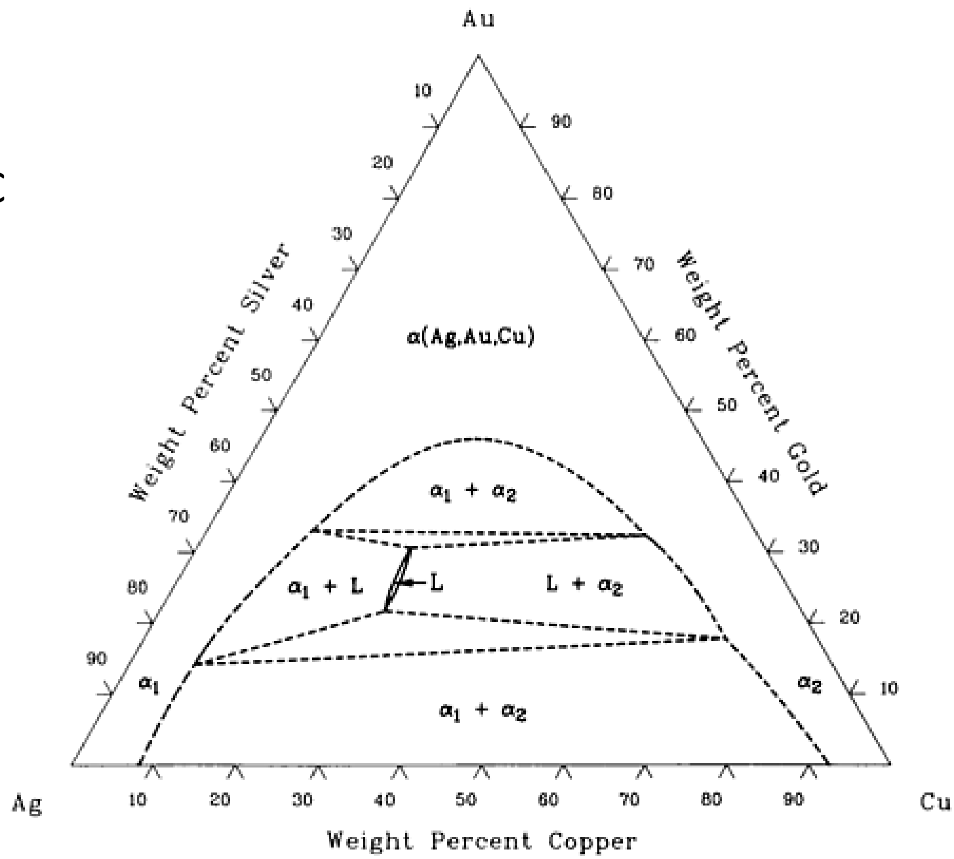
950 °C



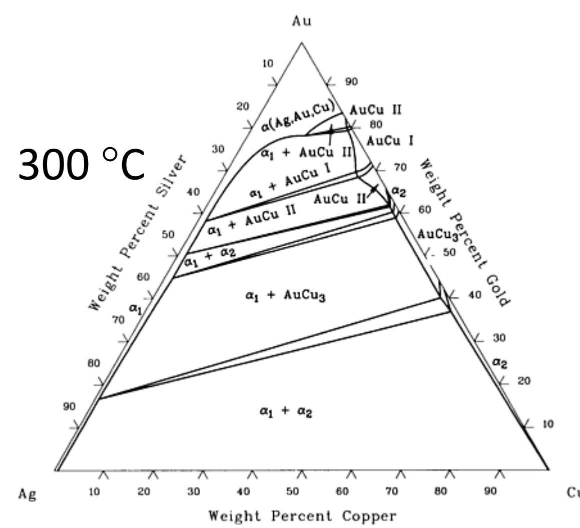
850 °C



775 °C

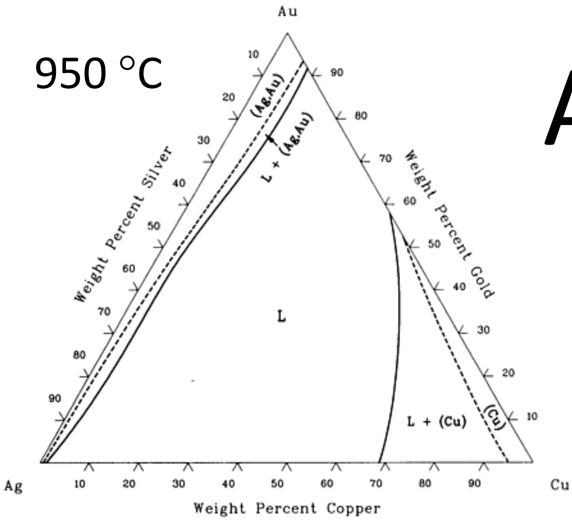


300 °C

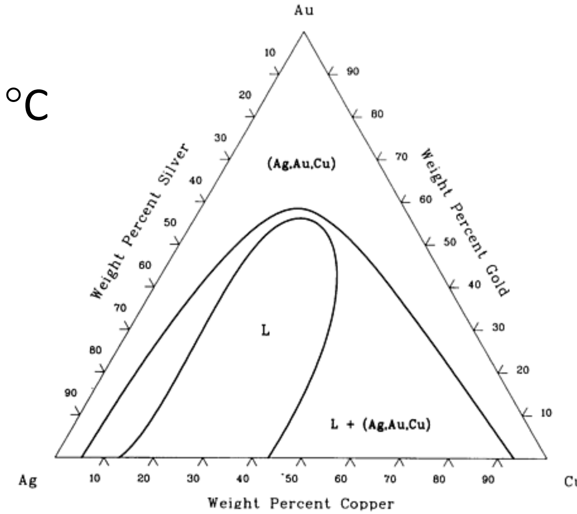


Ag-Au-Cu

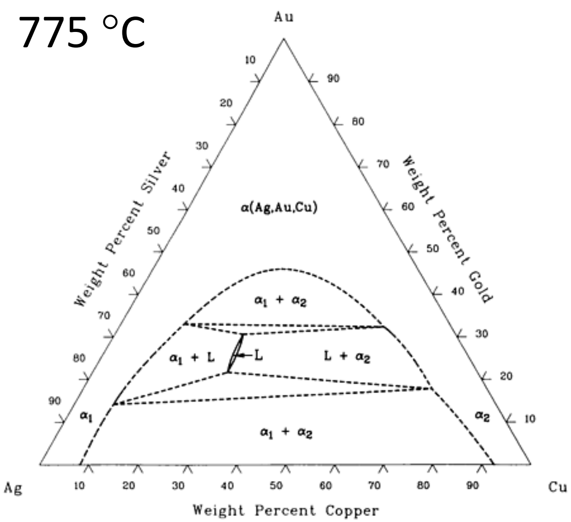
950 °C



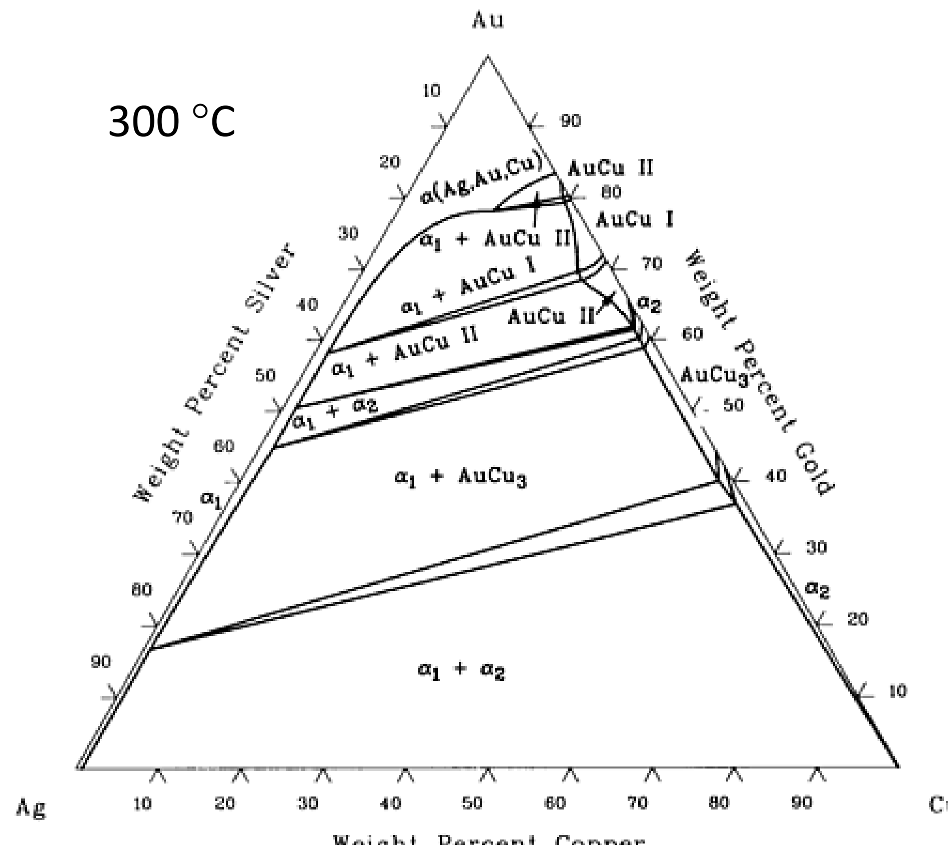
850 °C

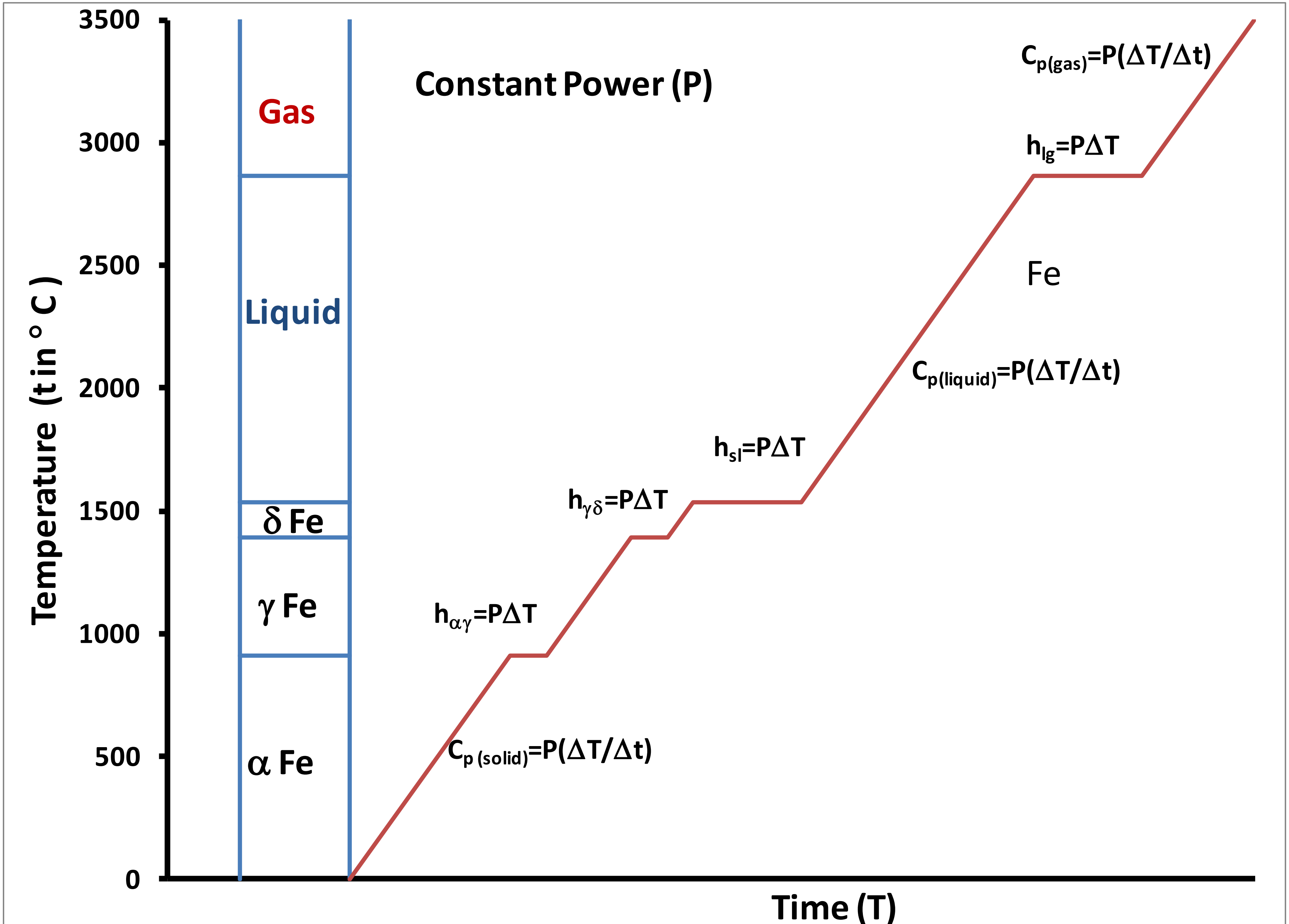


775 °C



300 °C





Constant Power (P)
Gas
Liquid
δ Fe
γ Fe
α Fe
Fe
$C_{p(gas)}=P(\Delta T/\Delta t)$
$h_{lg}=P\Delta T$
$C_{p(liquid)}=P(\Delta T/\Delta t)$
$h_{sl}=P\Delta T$
$h_{\gamma\delta}=P\Delta T$
$h_{\alpha\gamma}=P\Delta T$
$C_{p\ (solid)}=P(\Delta T/\Delta t)$
Temperature (t in ° C)
Time (T)
3500
3000
2500
2000
1500
1000
500
0

entropy

- statistical mechanics
  - **entropy** describes the number of the possible microscopic configurations of the system
  - statistical definition of entropy
  - more fundamental definition
  - all other definitions and all properties of entropy follow.
- thermodynamics **entropy**, (symbolized by *S)*
  - is a measure of the unavailability of a system's energy to do work
- measure of the randomness of molecules in a system
  - and is central to the second law of thermodynamics

enthalpy

- In thermodynamics and molecular chemistry, the **enthalpy** (denoted as *H*, *h*, or rarely as χ) is a quotient or description of thermodynamic potential of a system, which can be used to calculate the "useful" work obtainable from a closed thermodynamic system under constant pressure and entropy

Heats of reaction
enthalpy

- The total enthalpy of a system cannot be measured directly; the *enthalpy change* of a system is measured instead.
- Enthalpy change is defined by the following equation:

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

- where
  - ΔH is the *enthalpy change*
  - H_{final} is the final enthalpy of the system, measured in joules.
    - In a chemical reaction, H_{final} is the enthalpy of the products.
  - H_{initial} is the initial enthalpy of the system, measured in joules.
    - In a chemical reaction, H_{initial} is the enthalpy of the reactants.

Specific enthalpy

- The specific enthalpy of a working mass is a property of that mass used in thermodynamics, defined as where *u* is the specific internal energy, *p* is the pressure, and *v* is specific volume. In other words, $h = H / m$ where *m* is the mass of the system. The SI unit for specific enthalpy is joules per kilogram.

Physical Properties

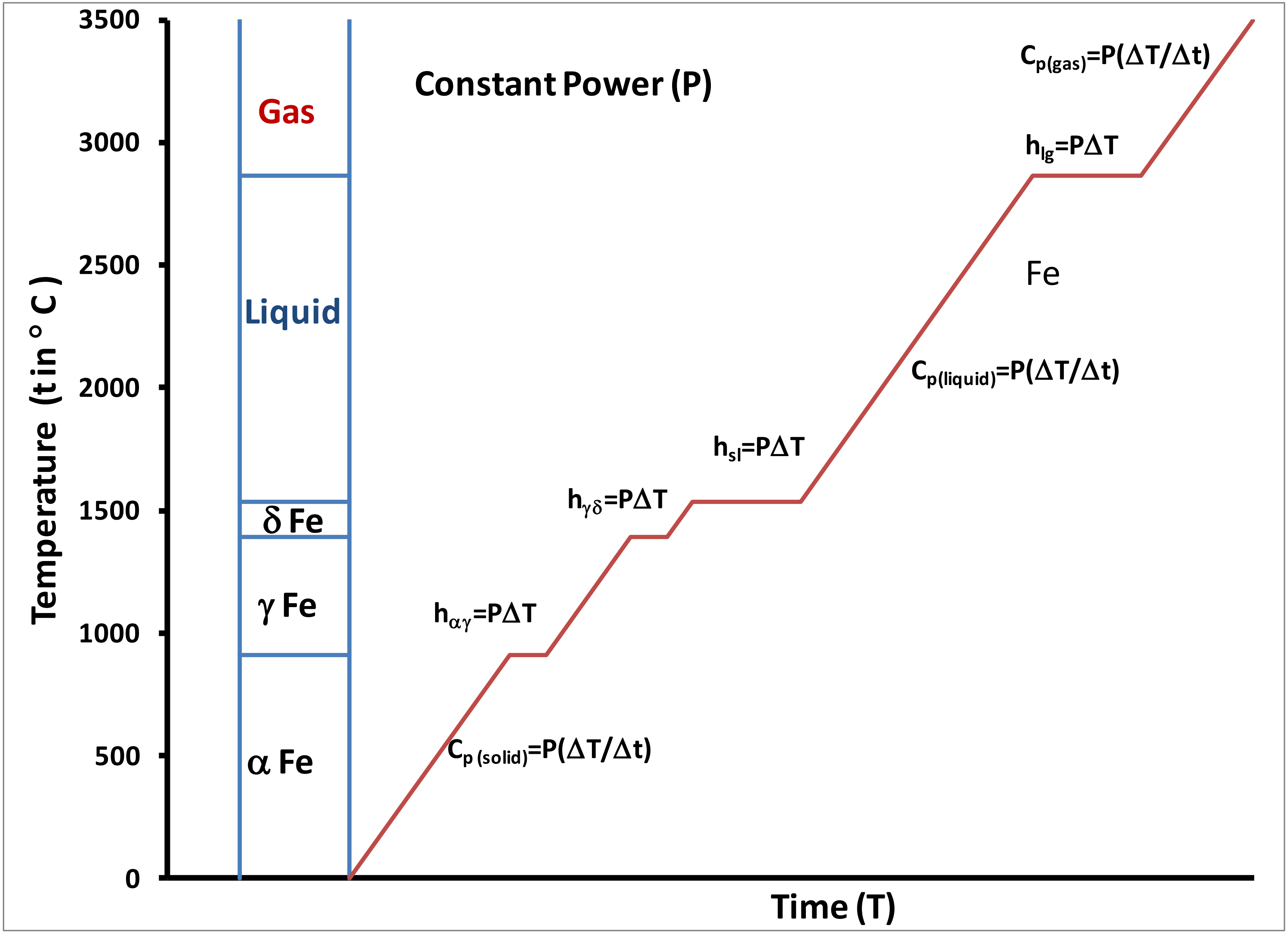
- **Standard enthalpy change of solution**
  - *“the enthalpy change observed in a constituent of a thermodynamic system, when one mole of an solute is dissolved completely in an excess of solvent under standard conditions.”*
- **Standard enthalpy change of fusion**
  - *“the enthalpy change required to completely change the state of one mole of substance between solid and liquid states under standard conditions.”*
- **Standard enthalpy change of vapourization**
  - *“the enthalpy change required to completely change the state of one mole of substance between liquid and gaseous states under standard conditions.”*
- **Standard enthalpy change of sublimation**
  - *“the enthalpy change required to completely change the state of one mole of substance between solid and gaseous states under standard conditions.”*
- **Lattice enthalpy**
  - “the enthalpy required to separate one mole of an ionic compound into separated gaseous ions to an infinite distance apart (meaning no force of attraction) under standard conditions.

exothermic reaction

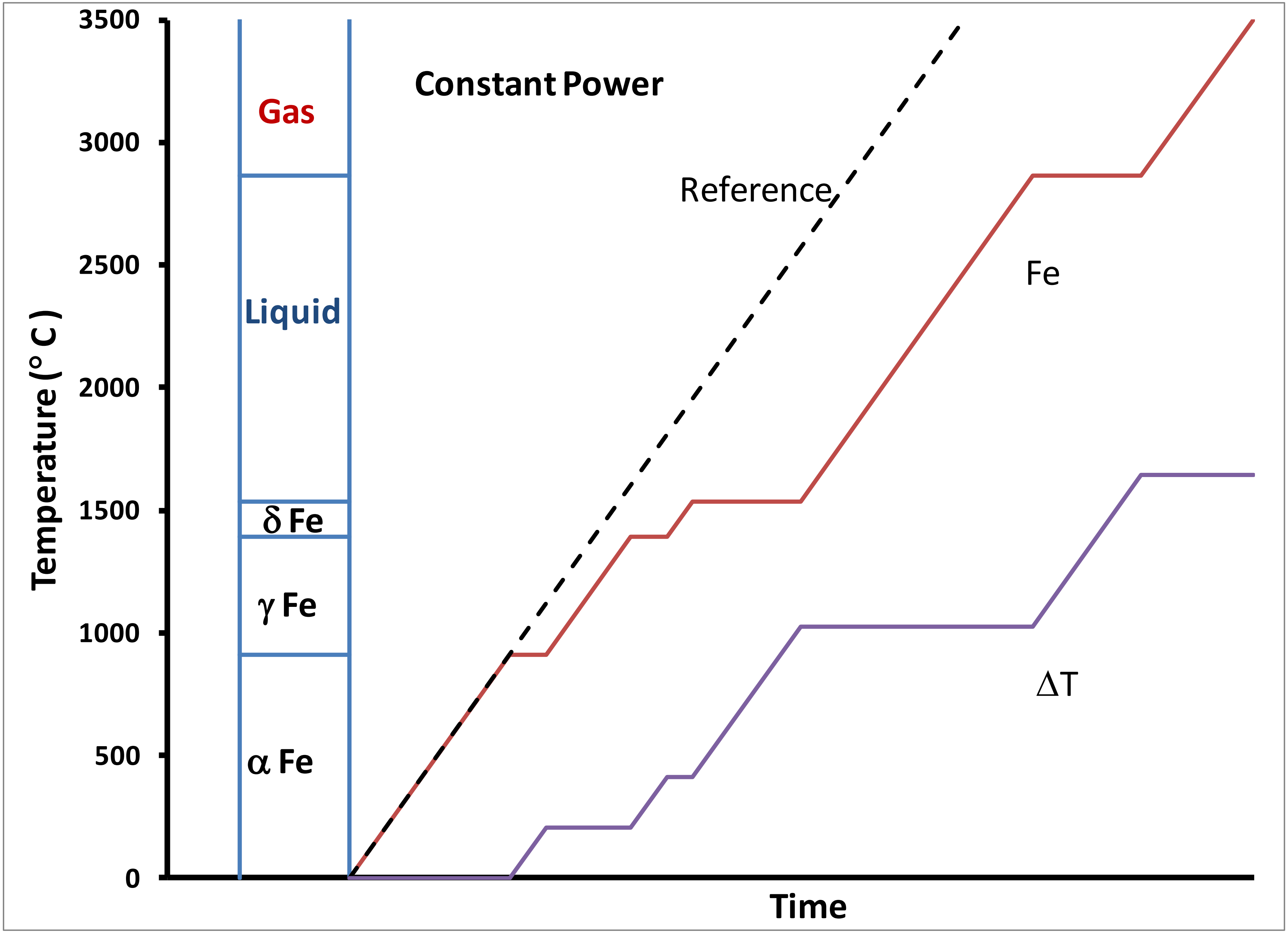
- For an exothermic reaction at constant pressure, the system's change in enthalpy is equal to the energy released in the reaction, including the energy retained in the system and lost through expansion against its surroundings.
- if ΔH is negative, the reaction is exothermic

Endothermic reaction

- for an endothermic reaction, the system's change in enthalpy is equal to the energy *absorbed* in the reaction, including the energy *lost by* the system and *gained* from compression from its surroundings
- If ΔH is positive, the reaction is endothermic

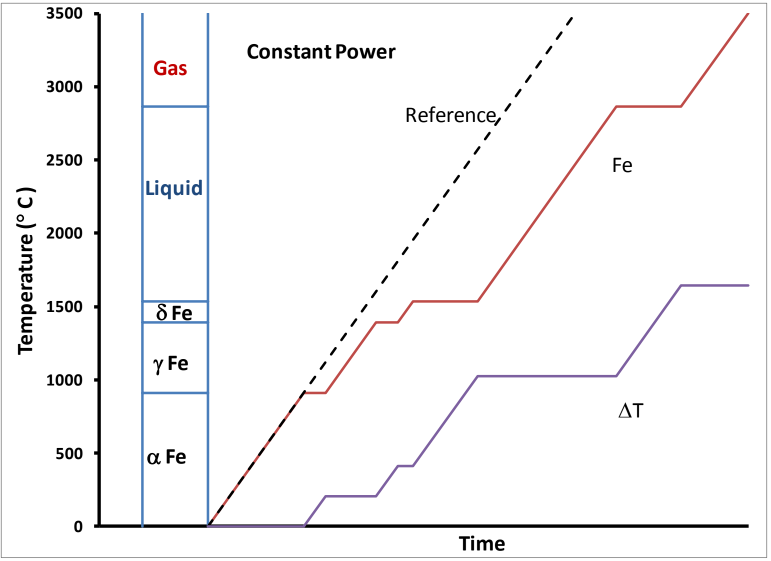


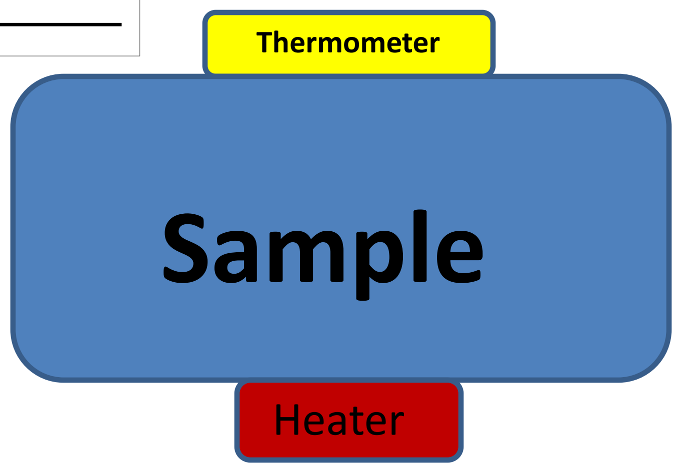
3500
3000
2500
2000
1500
1000
500
0
Temperature (t in ° C)
Time (T)
Constant Power (P)
Gas
Liquid
δ Fe
γ Fe
α Fe
Fe
$C_{p(gas)}=P(\Delta T/\Delta t)$
$h_{lg}=P\Delta T$
$C_{p(liquid)}=P(\Delta T/\Delta t)$
$h_{sl}=P\Delta T$
$h_{\gamma\delta}=P\Delta T$
$h_{\alpha\gamma}=P\Delta T$
$C_{p\ (solid)}=P(\Delta T/\Delta t)$



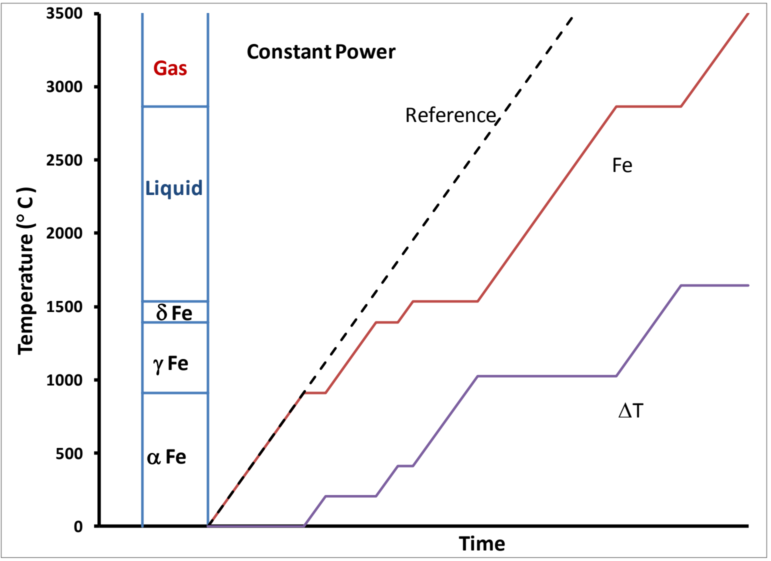
Constant Power
Gas
Liquid
δ Fe
γ Fe
α Fe
Reference
Fe
ΔT
Temperature (° C)
Time
3500
3000
2500
2000
1500
1000
500
0

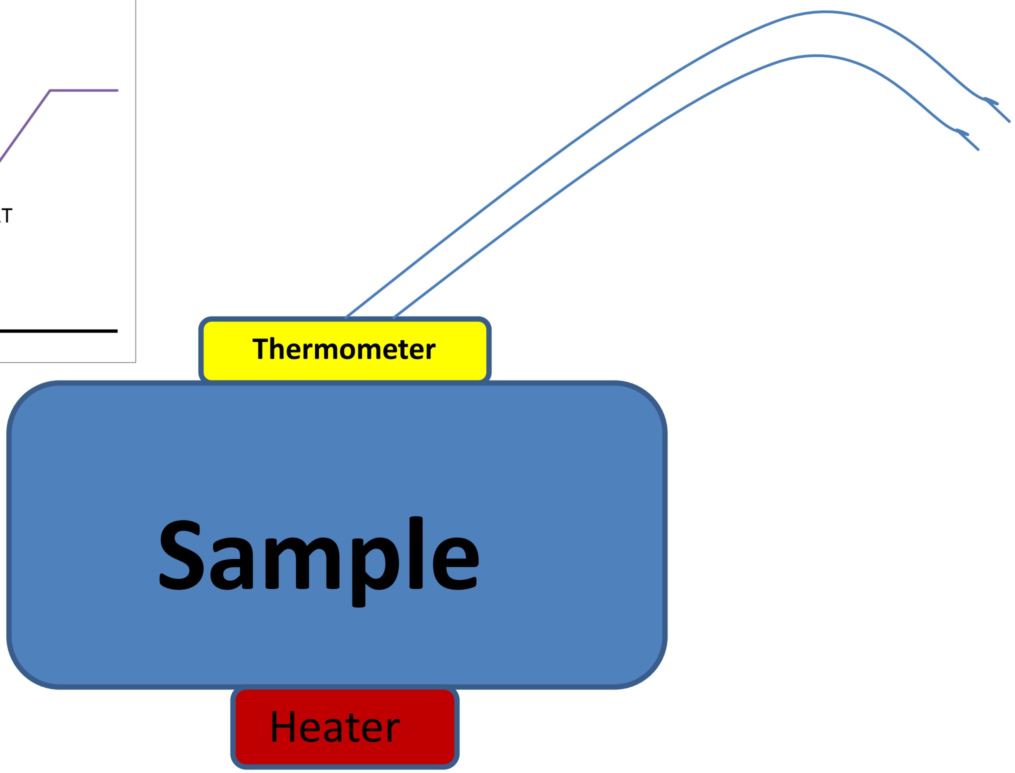
Measurement



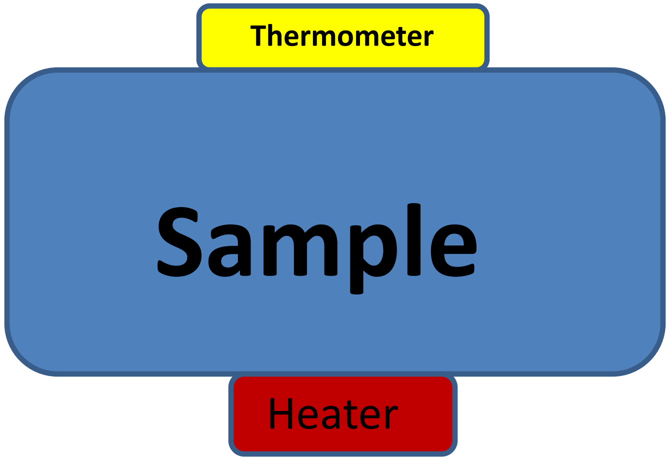


Measurement



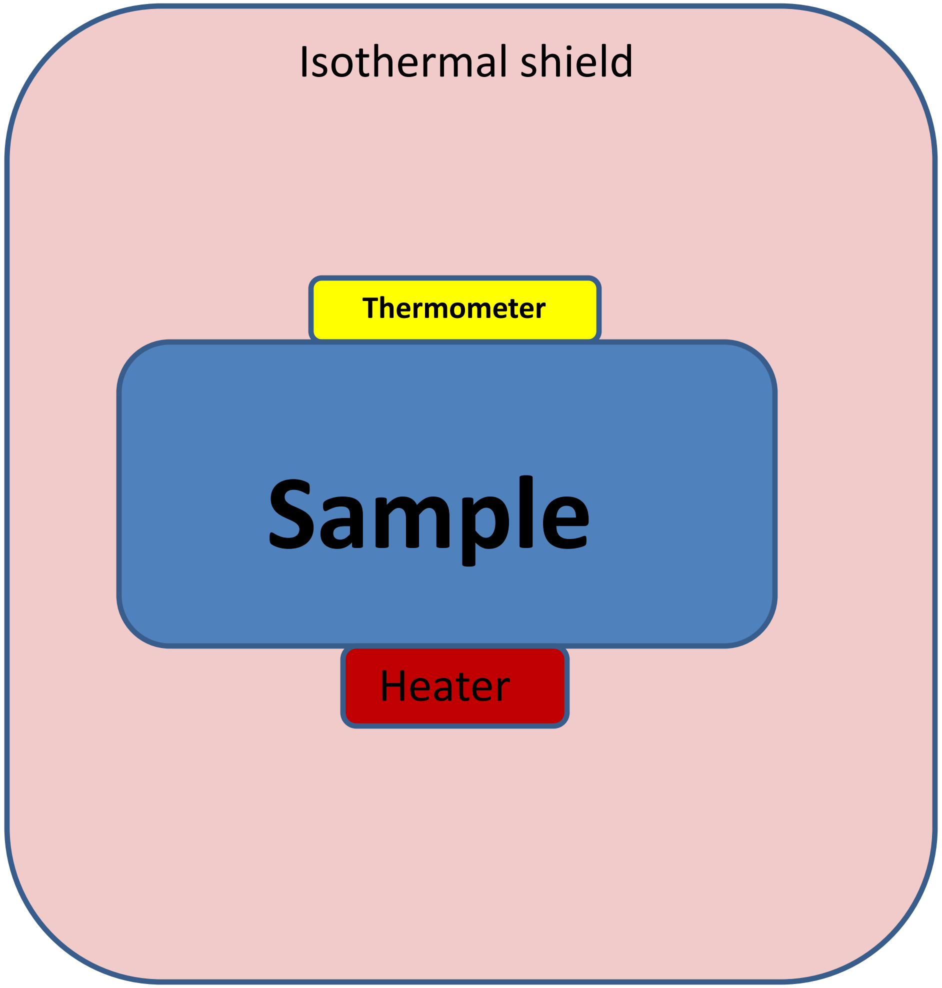


Measurement

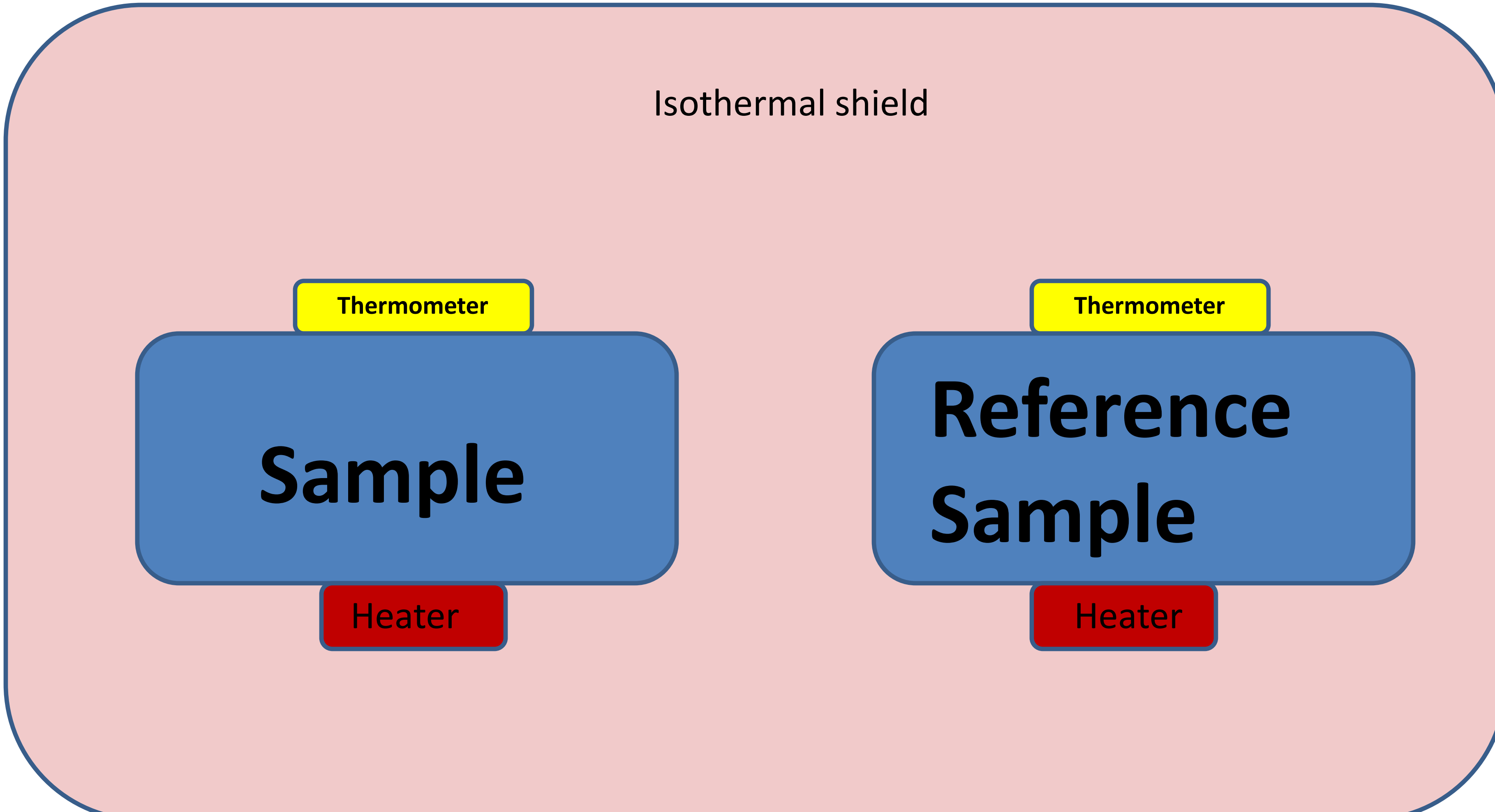


- Unaccounted for heat flow
  - Convection
  - Conduction
    - Heater wires
    - Thermometer wires
    - Support structure
  - Radiation
- Unaccounted for heat capacity
  - Heater
  - Heater wires
  - Thermometer
  - Thermometer wires
  - Support structure

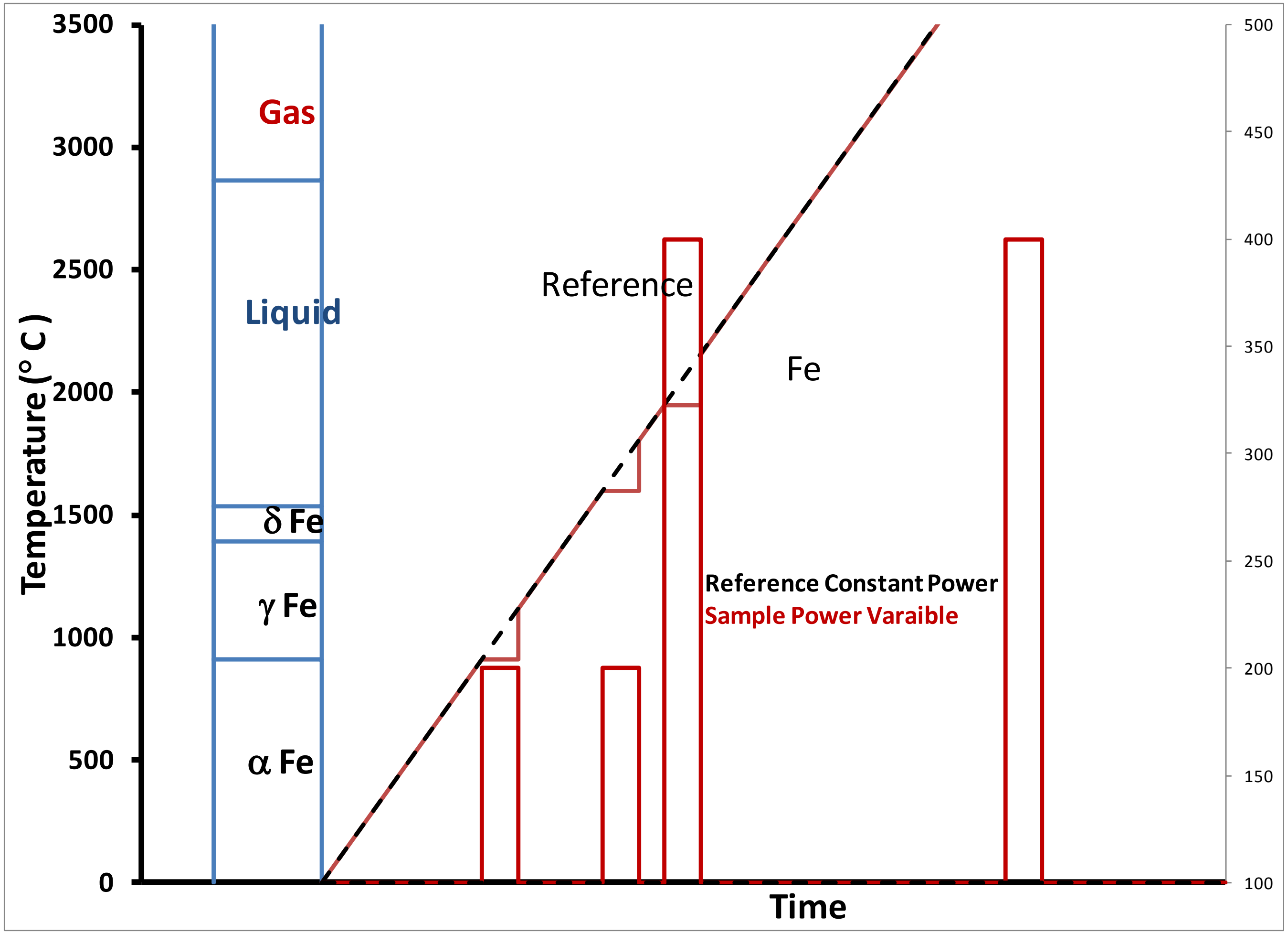
Semi adiabatic



Differential Calorimeter

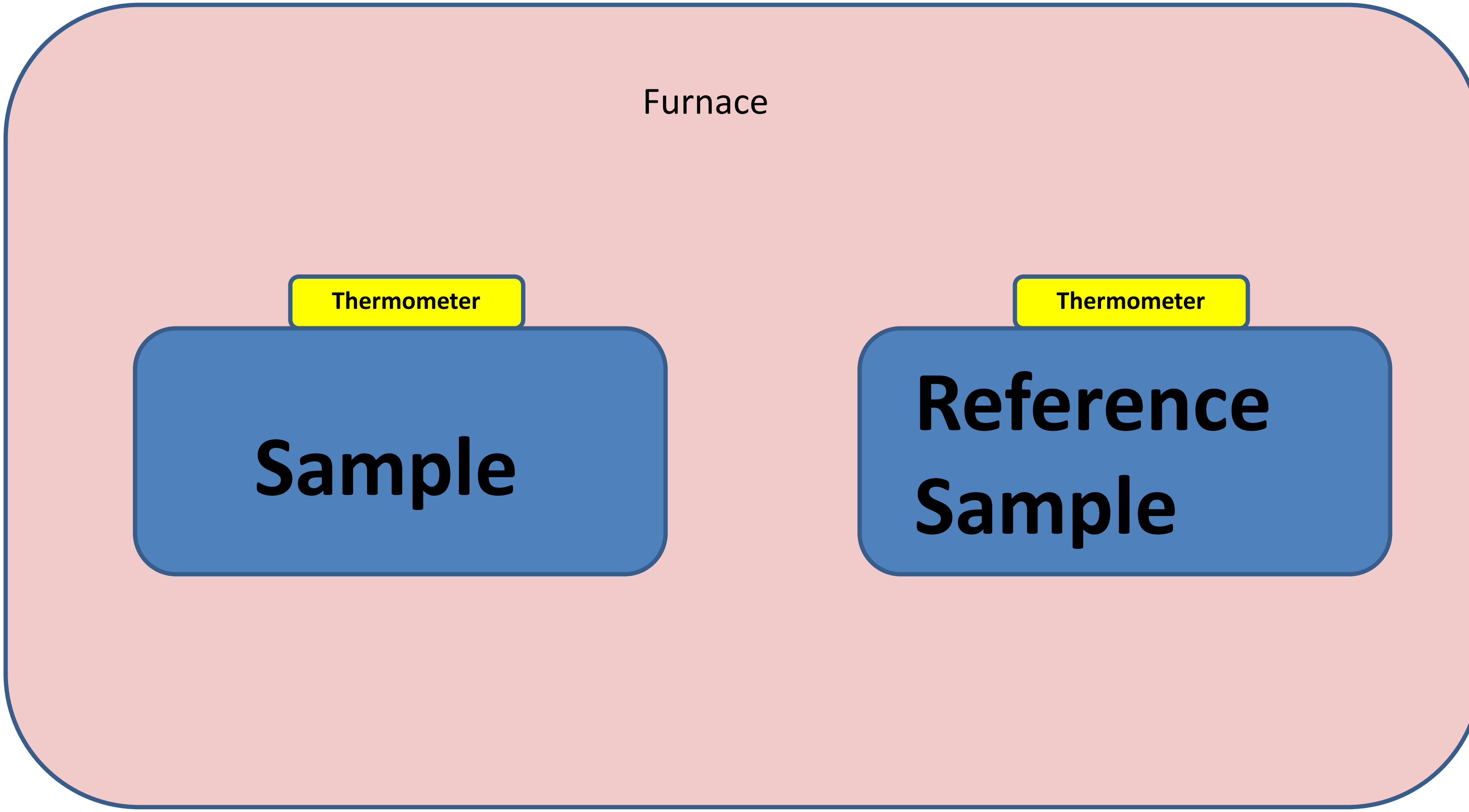


DSC

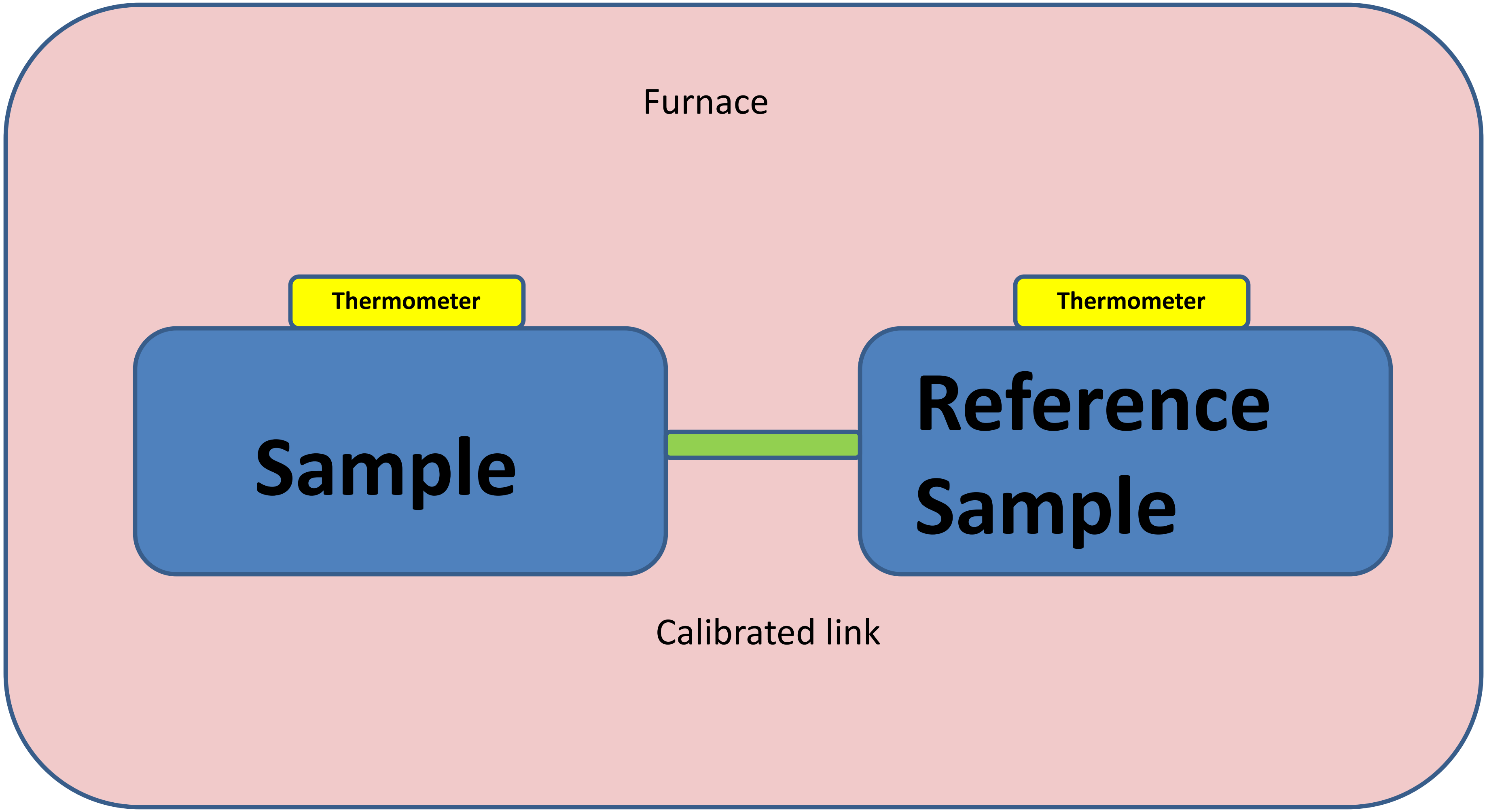


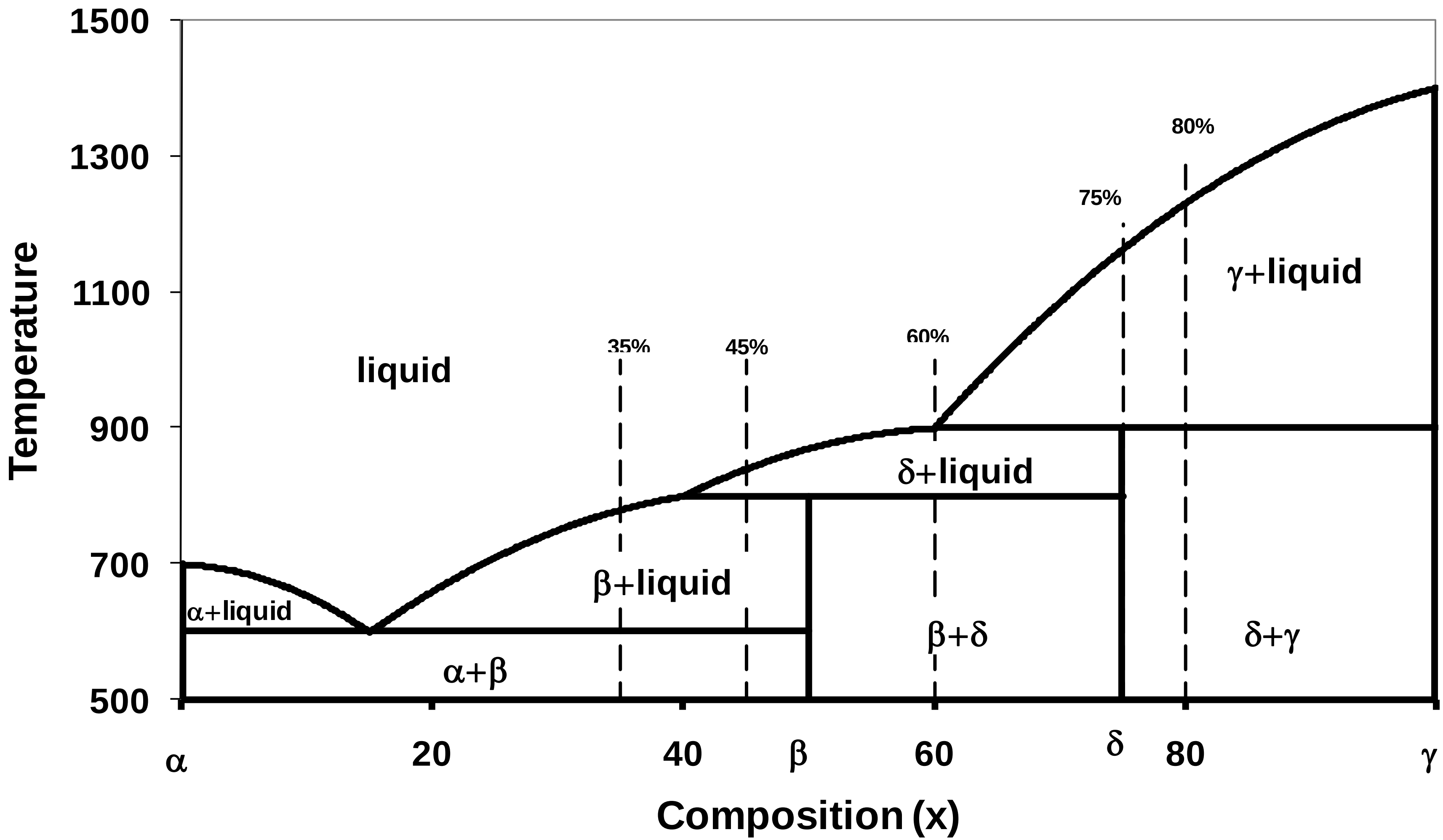
3500
3000
2500
2000
1500
1000
500
0
Temperature (° C)
Gas
Liquid
δ Fe
γ Fe
α Fe
Reference
Fe
Reference Constant Power
Sample Power Varaible
Time
500
450
400
350
300
250
200
150
100

Differential Thermal Analysis

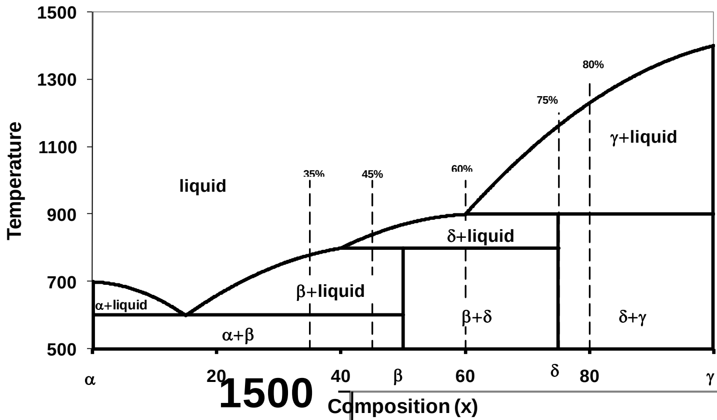


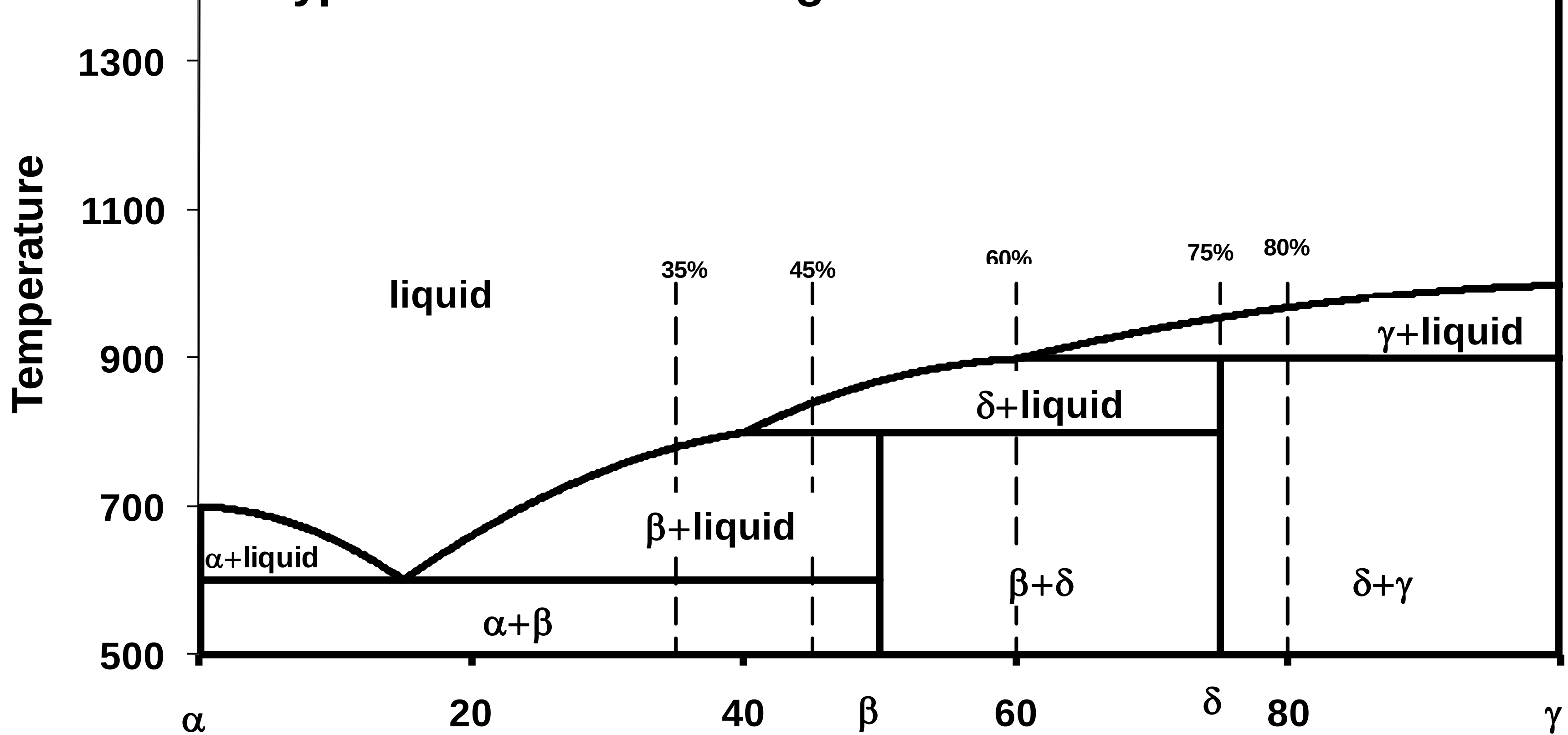
Differential Heat Flux Calorimeter

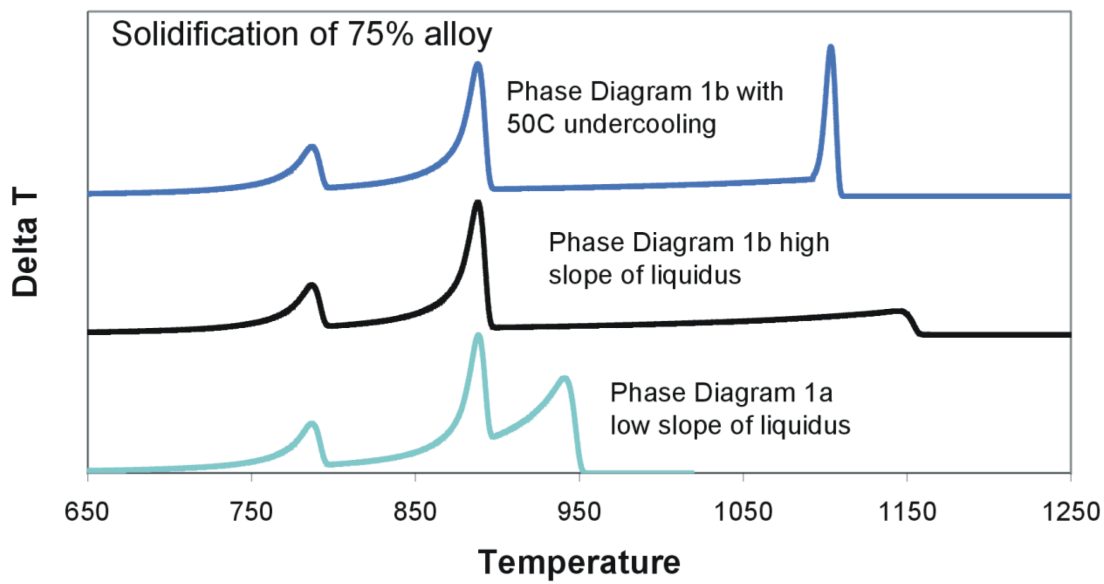



1500
1300
1100
900
700
500
Temperature
80%
75%
γ+liquid
35%
45%
60%
liquid
δ+liquid
β+liquid
α+liquid
β+δ
δ+γ
α+β
α
20
40
β
60
δ
80
γ
Composition (x)

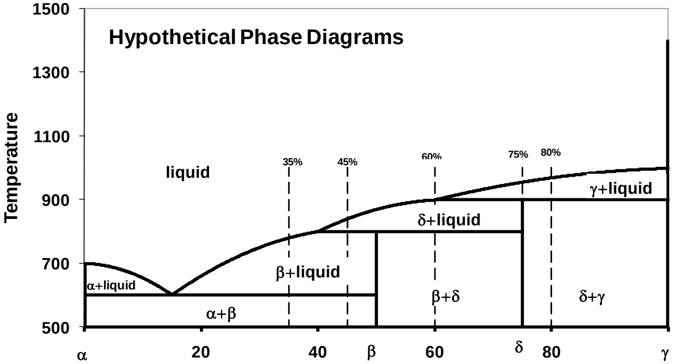
Hypothetical Phase Diagrams



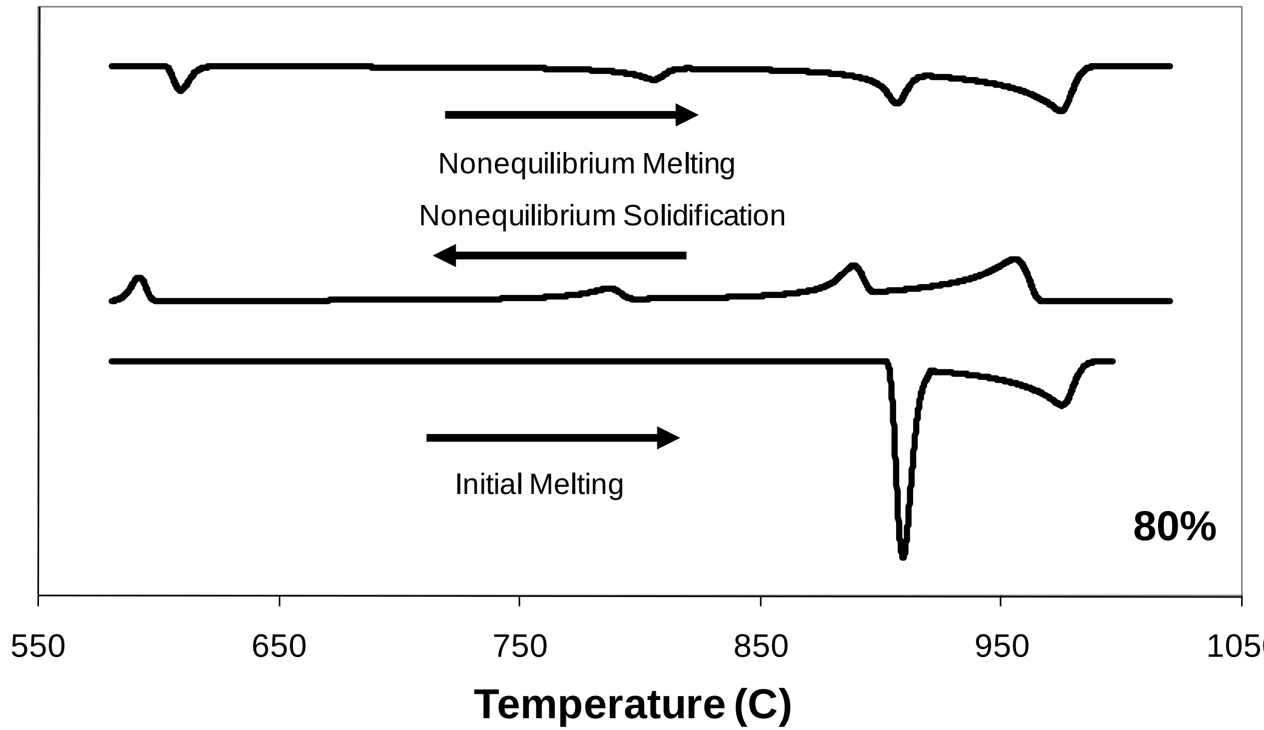




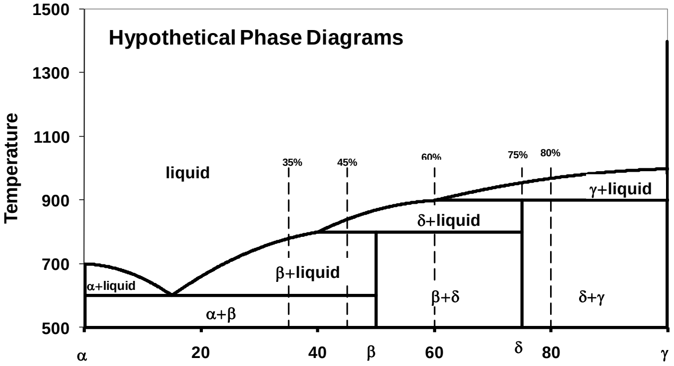
Solidification of 75% alloy
Phase Diagram 1b with
50C undercooling
Phase Diagram 1b high
slope of liquidus
Phase Diagram 1a
low slope of liquidus
Delta T
650
750
850
950
1050
1150
1250
Temperature



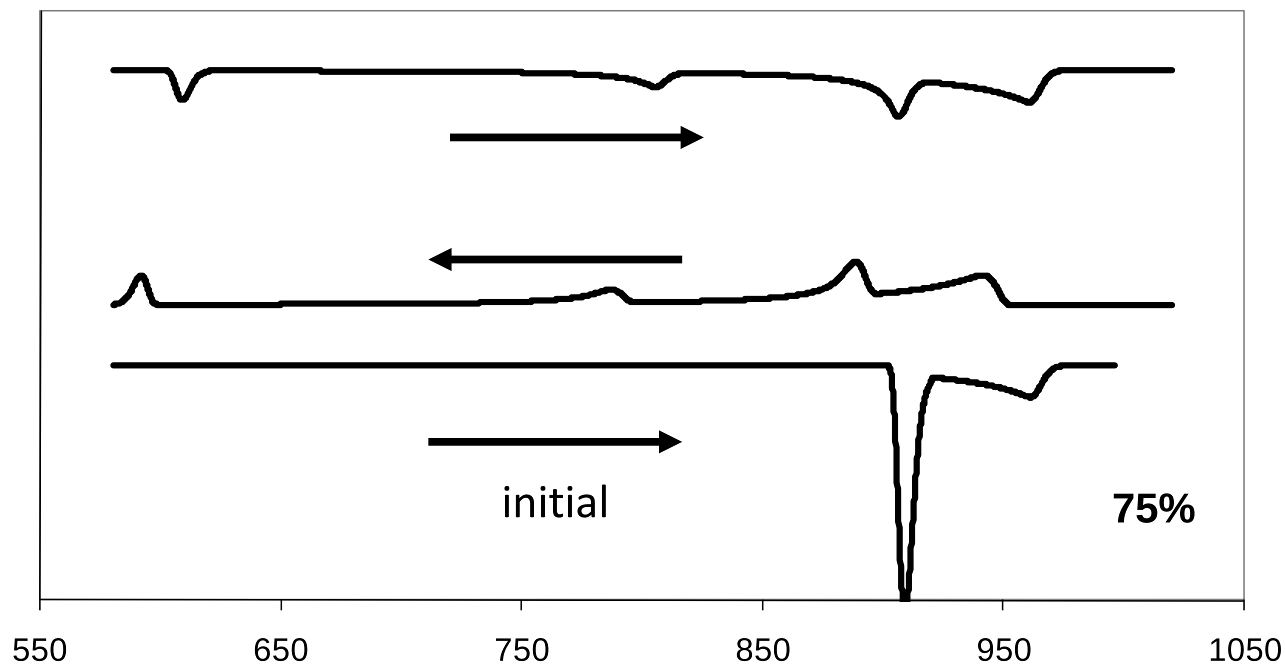
Hypothetical Phase Diagrams
Temperature
1500
1300
1100
900
700
500
liquid
35%
45%
60%
75%
80%
γ+liquid
δ+liquid
β+liquid
α+liquid
β+δ
δ+γ
α+β
α
20
40
β
60
δ
80
γ



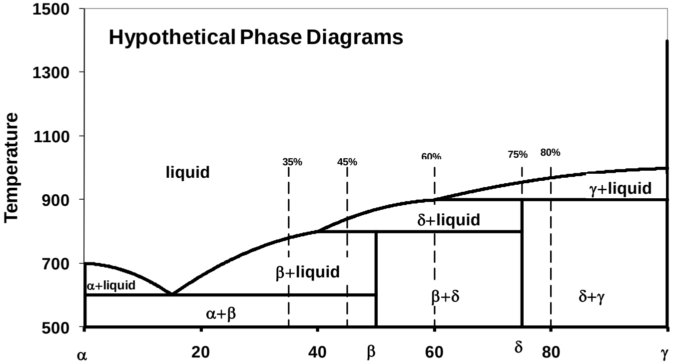
Nonequilibrium Melting
Nonequilibrium Solidification
Initial Melting
80%
550
650
750
850
950
1050
Temperature (C)



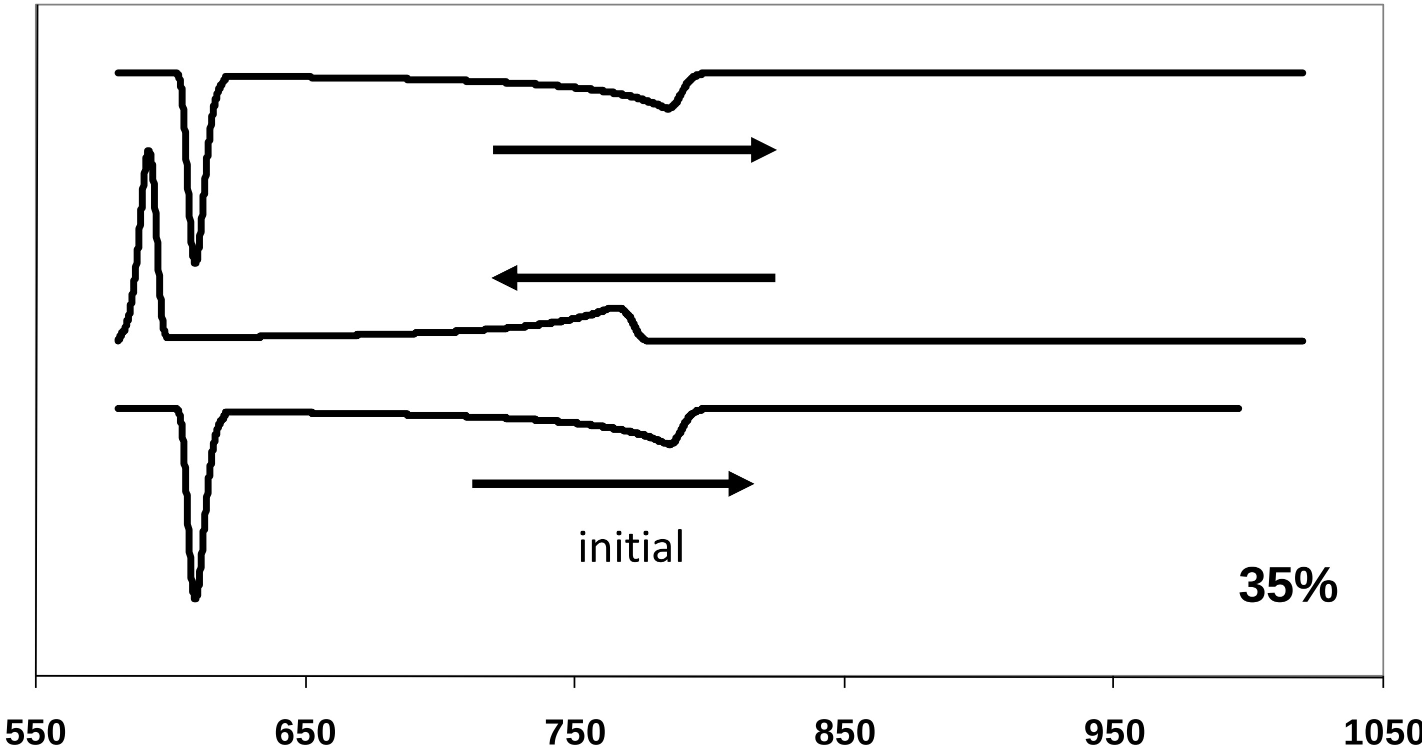
Hypothetical Phase Diagrams
Temperature
1500
1300
1100
900
700
500
liquid
35%
45%
60%
75%
80%
γ+liquid
δ+liquid
β+liquid
α+liquid
α+β
β+δ
δ+γ
α
20
40
β
60
δ
80
γ



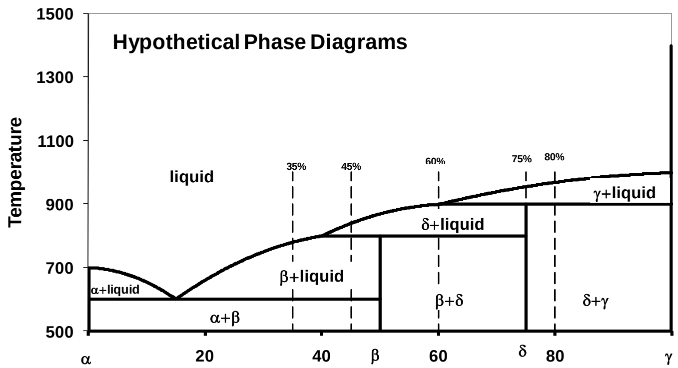
initial
75%
550
650
750
850
950
1050

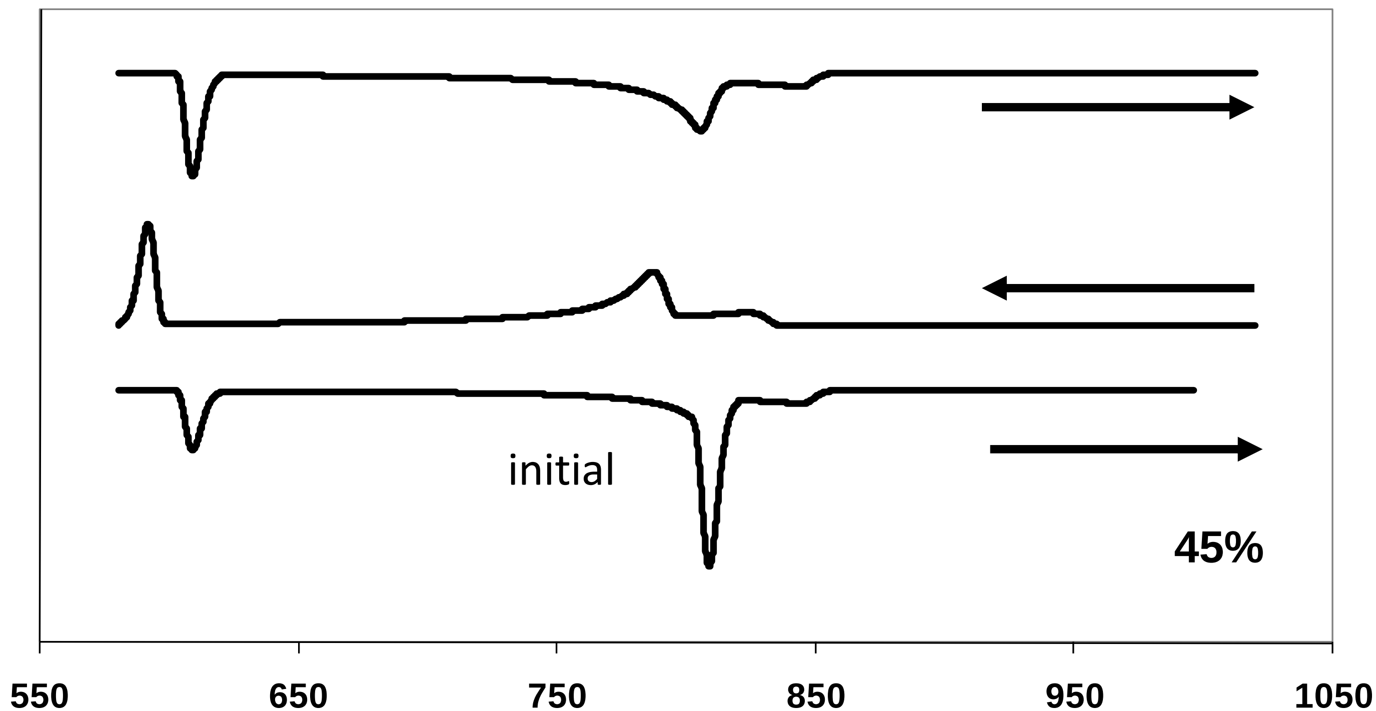


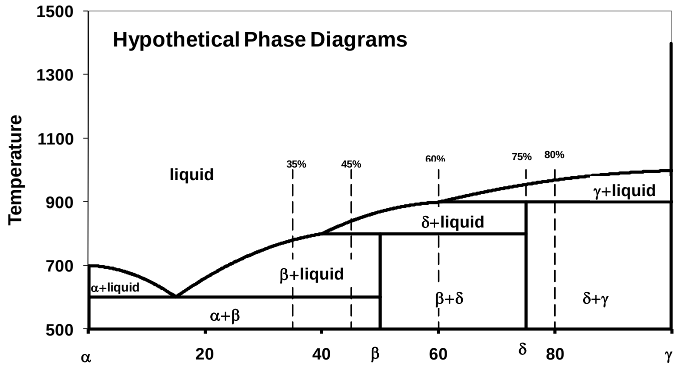
Hypothetical Phase Diagrams
Temperature
1500
1300
1100
900
700
500
liquid
35%
45%
60%
75%
80%
γ+liquid
δ+liquid
β+liquid
α+liquid
β+δ
δ+γ
α+β
α
20
40
β
60
δ
80
γ



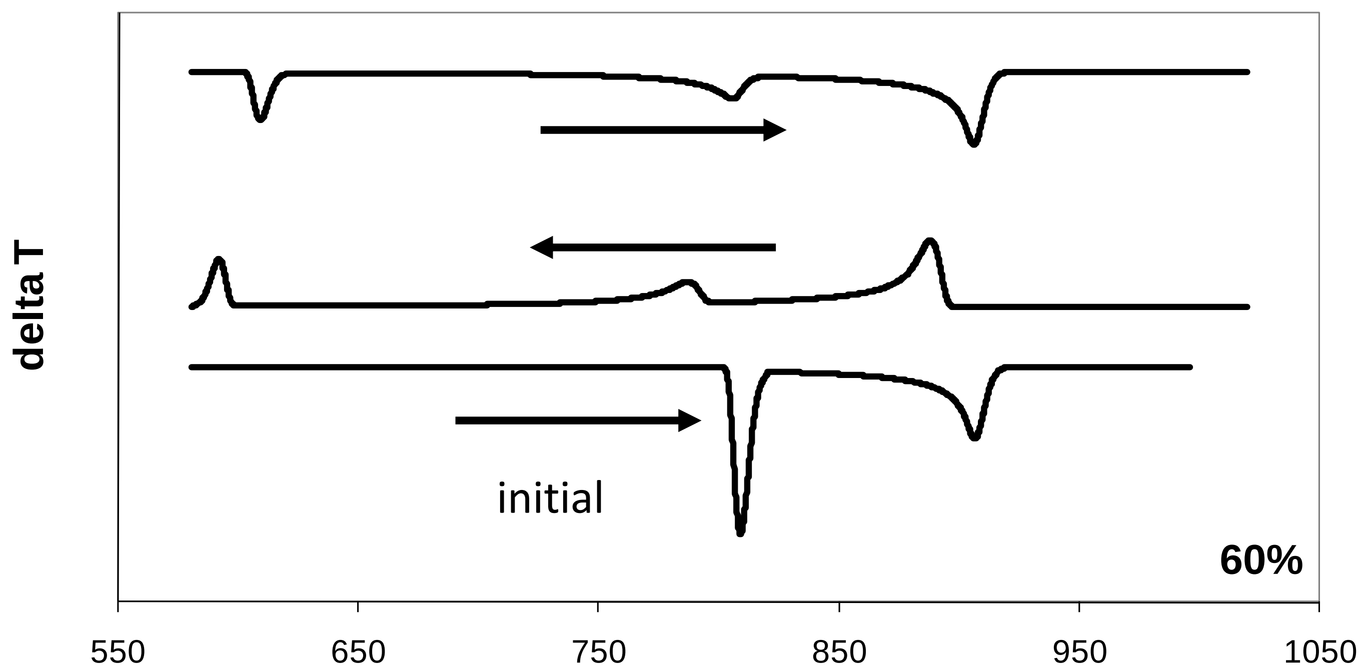
initial
35%
550
650
750
850
950
1050


Hypothetical Phase Diagrams
1500
1300
1100
900
700
500
Temperature
liquid
35%
45%
60%
75%
80%
γ+liquid
δ+liquid
β+liquid
α+liquid
β+δ
δ+γ
α+β
α
20
40
β
60
δ
80
γ


initial
45%
550
650
750
850
950
1050



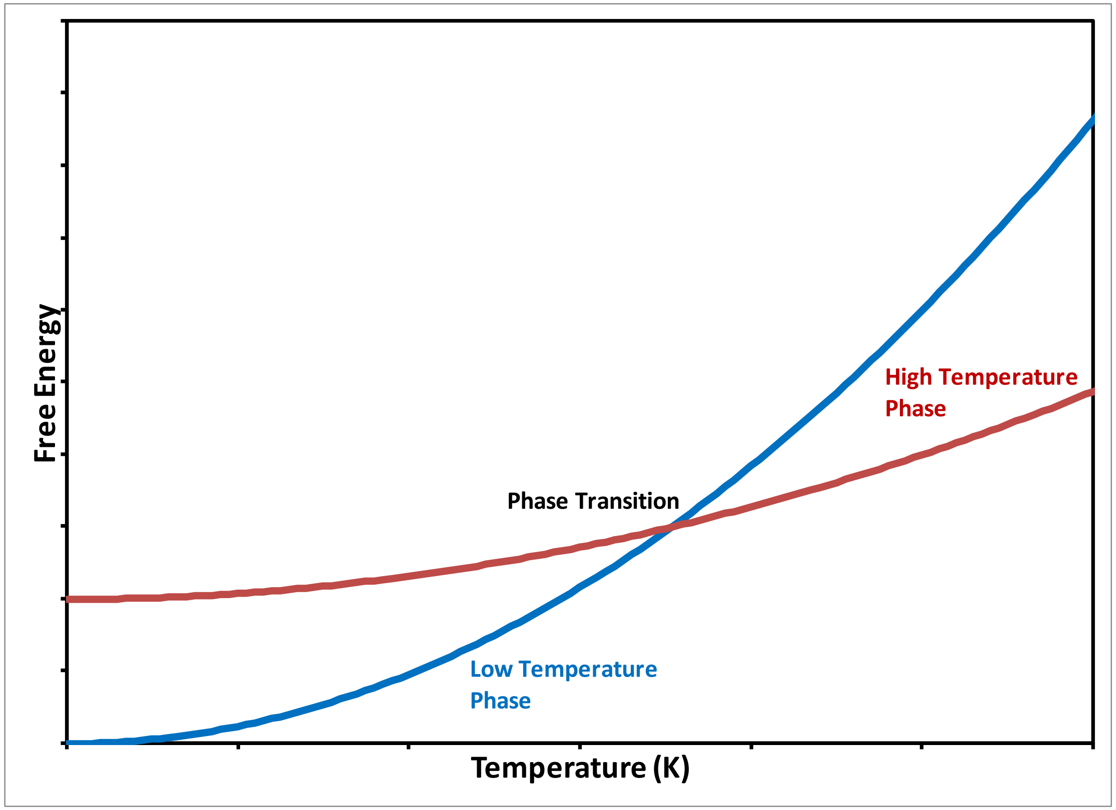
Hypothetical Phase Diagrams
Temperature
1500
1300
1100
900
700
500
liquid
35%
45%
60%
75%
80%
γ+liquid
δ+liquid
β+liquid
α+liquid
β+δ
δ+γ
α+β
α
20
40
β
60
δ
80
γ



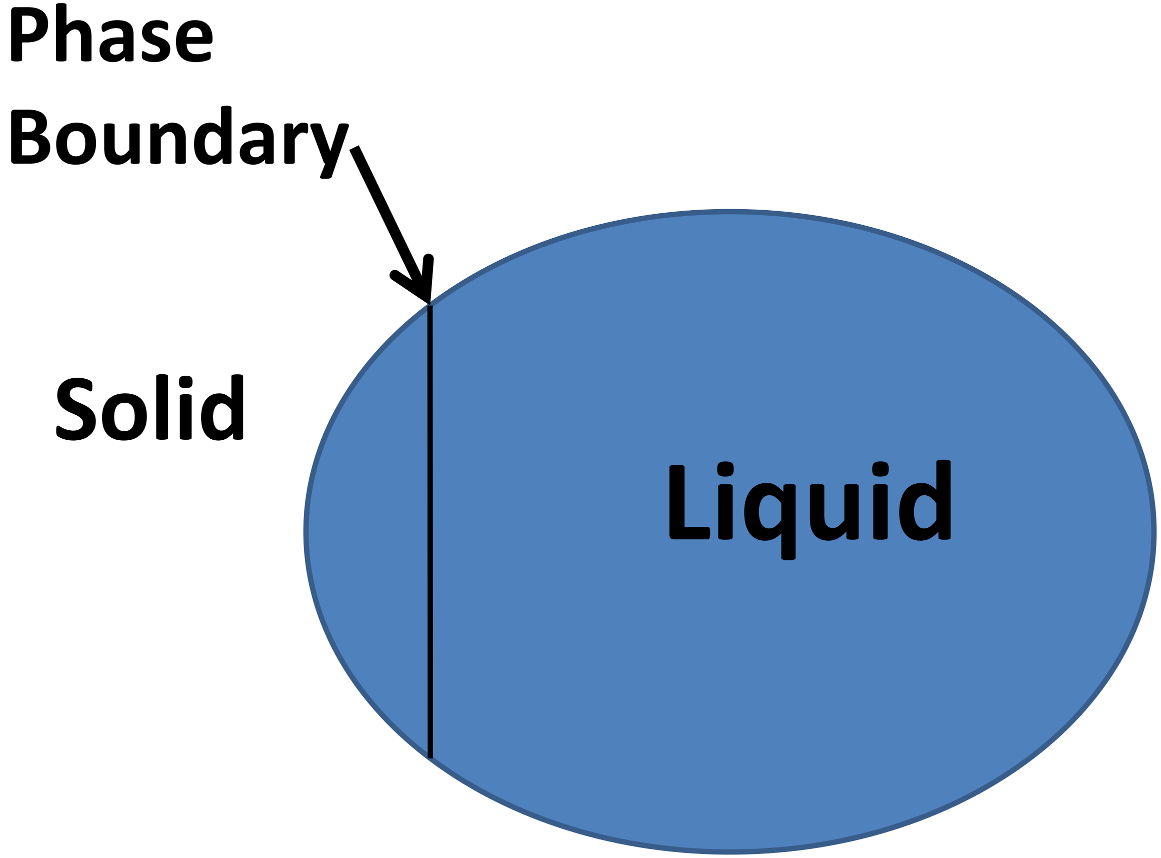
delta T
initial
60%
550
650
750
850
950
1050

Phase Transition

- At phase-transition point
  - the two phases have identical free energies
  - equally likely to exist.
- Below the phase-transition point
  - Low temperature phase is more stable state of the two.
- Above the phase-transition point
  - High temperature phase is more stable state of the two.



Nucleation



Phase Transition

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  - the two phases have identical free energies
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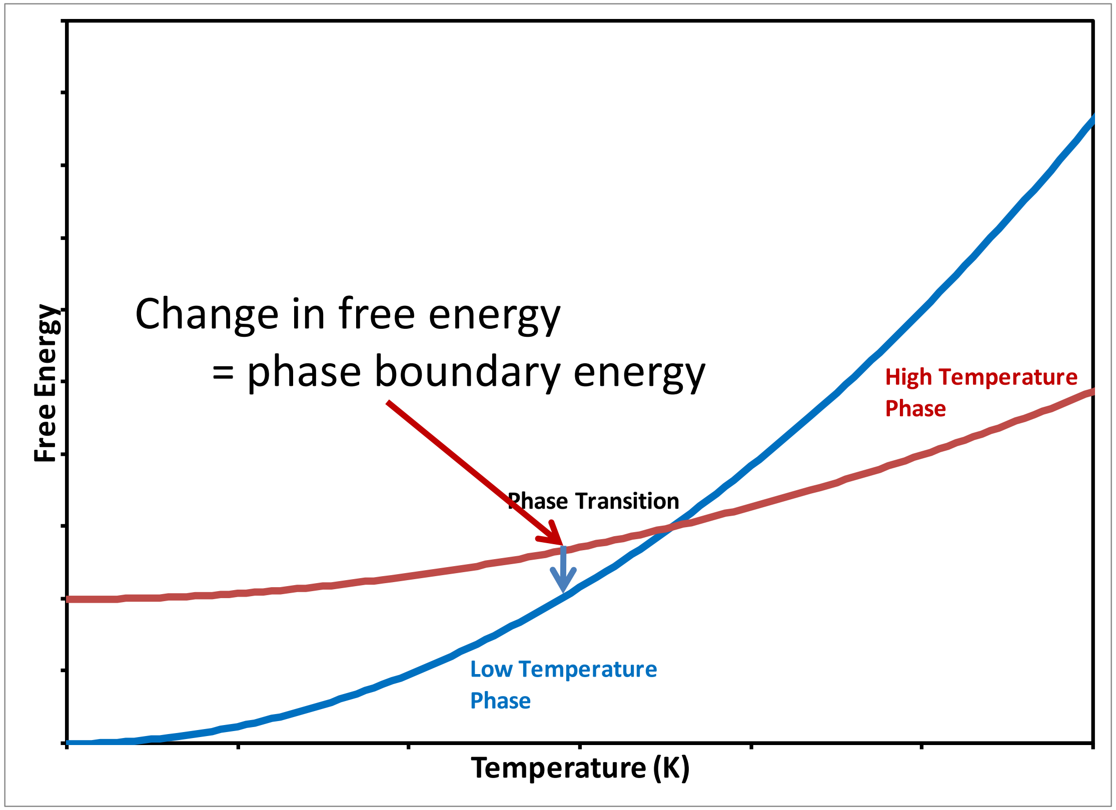
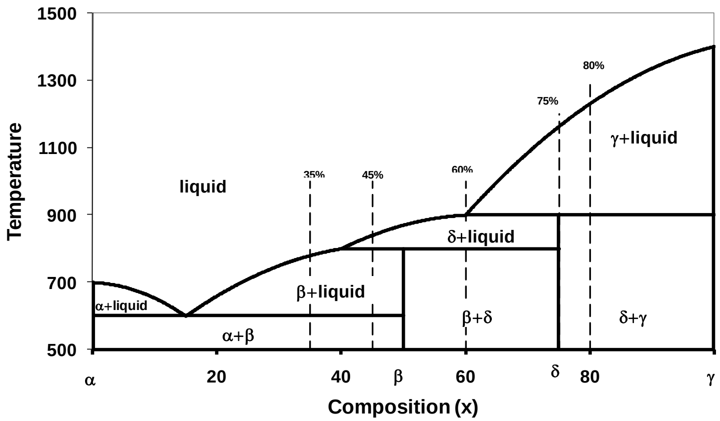
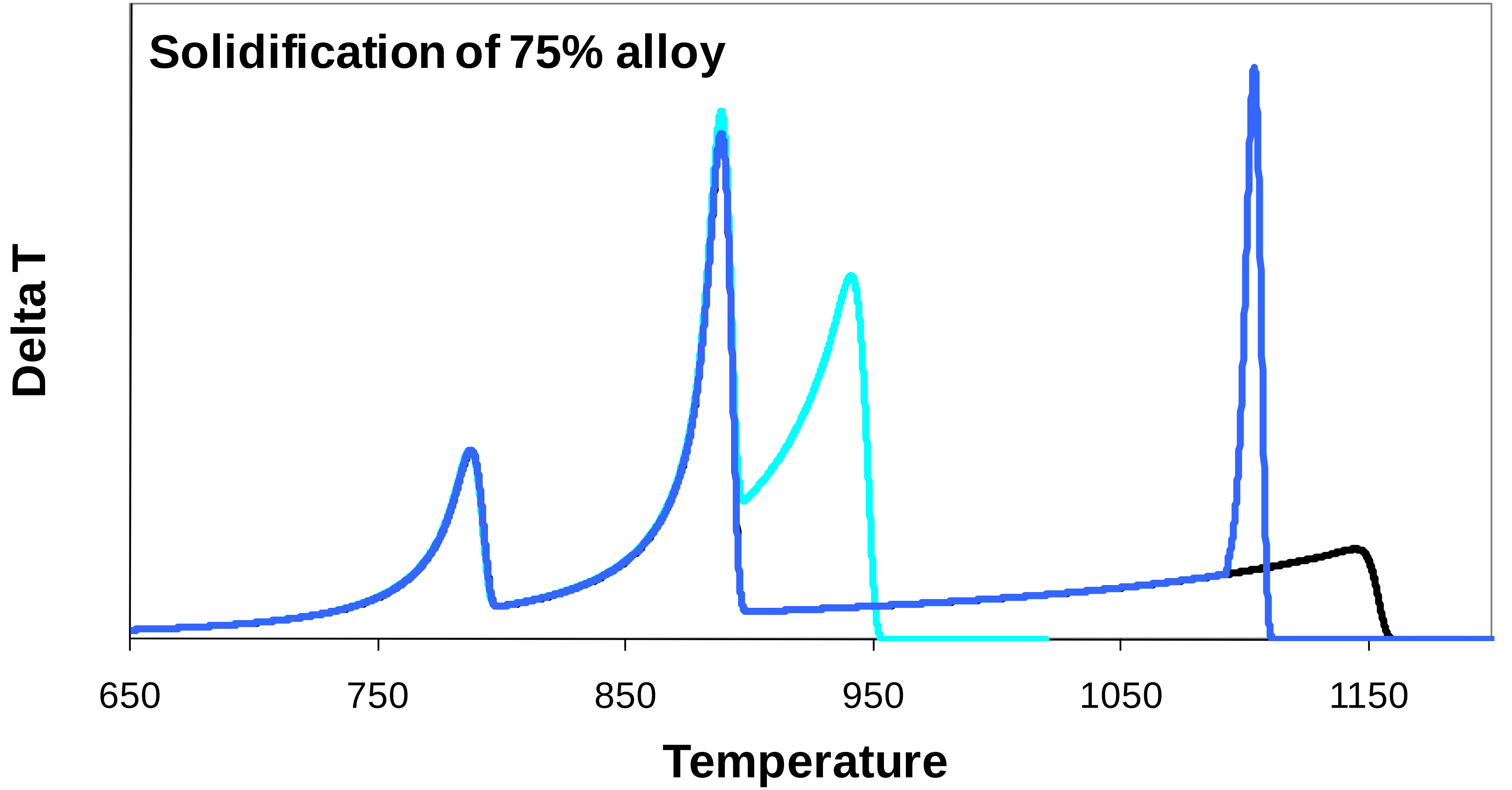




undercooling



Types of thermal analysis

- Semi Adiabatic Specific Heat
- **DTA** differential thermal analysis (rt to 1650 °C)
- **DSC** Differential Scanning Calorimetry (rt to 750 °C)
- **Heat flux DSC** (rt to 1650 °C), (-150 to 900 °C)
- **TGA** thermal gravimetric analysis (rt – 1500 °C)
- **STA** simultaneous thermal analysis (rt – 1500 °C)
- **TMA**
  - thermo mechanical analysis
  - Thermo magnetic analysis
- Dilatometry (thermal expansion)
  - (rt to 1650 °C), (-150 to 900 °C)

NIST Recommended Practice Guide Special Publication 960-15

- **DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing**
  - W. J. Boettinger, U. R. Kattner, K.-W. Moon
    - Metallurgy Division
    - Materials Science and Engineering Laboratory,
    - National Institute of Standards and Technology
  - J. H. Perepezko
    - Department of Materials Science and Engineering,
    - University of Wisconsin - Madison
  - Special Publications
  - November 2006
  - **U.S. Department of Commerce**

Terms and definitions

- ASTM E473, "Standard Terminology Relating to Thermal Analysis," is a compilation of definitions of terms used in other ASTM documents on all thermal analysis methods including techniques besides DTA and HF-DSC.
- ASTM E1142, "Terminology Relating to Thermophysical Properties," is a compilation of definitions of terms used in other ASTM documents that involve the measurement of thermophysical properties in general.

ASTM Practice Standards

- ASTM E967, "Practice for Temperature Calibration of DSC and DTA," presents simple recipes for calibration for fixed mass and heating rate using two pure materials to obtain a linear correction for conversion of measured temperature to actual temperature. The onset temperature extracted from the melting peak is determined by the extrapolation method, see section 2.4.3. For some ♦DTA and Heat-flux DSC Measurements 5 materials the standard suggests using the peak for calibration, a method not recommended for metals.
- ASTM E968, "Standard Practice for Heat Flow Calibration of DSC," uses sapphire as heat capacity standard. The method is described in section 2.4.4.
- ASTM E2253, "Standard Method for Enthalpy Measurement Validation of Differential Scanning Calorimeters," presents a method using three small masses to determine the detection limit of DTA/DSC.

ASTM Practice Standards

- ASTM E928, "Standard Test Method for Determining Purity by DSC," employs comparison of the shape of the melting peak of an impure sample to the shape for a high purity sample to determine the concentration of the impurity. The method uses the "1/F plot" which examines the down slope of the melting peak.
- ASTM E794, "Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis," employs the extrapolated onset determination method.
- ASTM E793, "Standard Test Method for Enthalpies of Fusion and Crystallization by DSC," uses area on signal vs. time plot for comparison to known heats of fusion of pure materials.
- ASTM E1269, "Standard Test Method for Determining Specific Heat Capacity by DSC," uses sapphire or aluminum as a standard.